ABSTRACT

Title of Thesis: IMPACT OF SURFACE APPLICATION OF FLUE GAS DESULFURIZATION GYPSUM ON INFILTRATION, PHOSPHORUS BEHAVIOR, AND TOTAL SULFUR IN A PREVIOUSLY MANURED COASTAL PLAIN SOIL

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Flue gas desulfurization (FGD) gypsum was surface-applied on a poorly drained cultivated Coastal Plain soil in Maryland containing excessive amounts of plant-available phosphorus (P). Using a constant head double-ring infiltrometer, a field experiment indicated a slight increase in final infiltration rate (FIR) at 10 and 15 Mg ha^{-1} application rates, however a laboratory rainfall simulation showed no significant effect of FGD gypsum on FIR. Water extractable phosphorus (WEP) decreased by 13-47% one year after application of FGD gypsum. Linear relationships were established between Mehlich 3 (M3) and ammonium oxalate extractions of P and aluminum (Al) (r^2 = 0.83, 0.56, respectively), supporting previous research on the reliability of M3 in place of ammonium oxalate to predict P loss. One year after FGD gypsum application total S was 3-150% higher at 15 cm and 44-74% higher at 30 cm depths. No significant difference in total S was apparent at deeper depths.

IMPACT OF SURFACE APPLICATION OF FLUE GAS DESULFURIZATION GYPSUM ON INFILTRATION, PHOSPHORUS BEHAVIOR AND TOTAL SULFUR IN A PREVIOUSLY MANURED COASTAL PLAIN SOIL

By

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TABLE OF ABBREVIATIONS & SYMBOLS

Table 1. Symbols used in text

Symbol	Definitions	Units
α	Saturation factor representing Al and Fe oxides available for P sorption	ratio
Θ	Volumetric water content	cm^3/cm^3
C	Equilibrium concentration: Langmuir and Freundlich sorption models	mg L^{-1}
CEC	Cation exchange capacity	(meq/100g)
DPS	Degree of P Saturation: relates soil P to available binding sites of soil Al and Fe	%
DPS_{ox}	DPS calculated by P,Al, Fe extraction in mmol kg-1	%
EC	Electrical conductivity	dS m^{-1}
ESP	Exchangeable Sodium Percentage	%
FGD	Flue gas desulfurization	
FIR	Final Infiltration Rate	mm h^{-1}
ICP	inductively coupled argon plasma spectrometry	
IR	Infiltration rate	mm h^{-1}
K	Langmuir binding coefficient	L mg^{-1}
LOI	Loss-on-ignition technique to assess soil carbon	%
M3	Mehlich 3 Extraction typically used in MD and DE to access plant available nutrients	mg kg^{-1} or mmol kg^{-1}
NRCS	Natural Resource Conservation Service (division of USDA)	
PG	Phosphogypsum	
PSC_t	Total Phosphorus Sorption Capacity (Pox + Smax)	mmol kg^{-1}
P_{sat}	Measure or proportion of sorbed P based on P sorption capacity (Al + Fe)	
PSU	Penn State University	
WQIA	Water Quality Improvement Act	
rpm	revolutions per minute	
Smax	Saturation factor for the Langmuir model indicating the probable max adsorbtion	mg kg^{-1}

	possible for a given chemical element	
STP	Soil Test Phophosrus: refers to a number of extractions used regions as indicators of plant-available (e.g. M1, M3, Olsen, Bray-1…)	Usually mg kg^{-1}
UDSTP	University of Delaware Soil Testing Program	
UMCP	University of Maryland- College Park	
USDA	United States Department of Agriculture	
WEP	Water Extractable Phosphorus	mg kg^{-1}
$\bar{x}$	sample mean	

CHAPTER ONE -- INTRODUCTION

Justification / Rationale

According to the World Resources Institute (2009) eutrophication has become one of the leading causes of water quality decline worldwide as the number of affected coastal and freshwater systems is anticipated to increase along with global population and energy use. Elevated nutrient-levels in the form of nitrogen (N) and P are widespread and difficult to trace, especially when entering waterways from diffuse non-point sources such as agriculture and urban life. Excess N and P promote algae proliferation, leading to diminished O_2 levels in aqueous environments; thus contributing to fish kills, loss of biodiversity and the obstruction of water use for multiple purposes, including drinking and recreation. According to Carpenter et al. (1998), 82% of P and 84% of N discharges are from non-point sources, and current trends anticipate this will increase due to increasing human populations that tax ecosystem health. The United States Environmental Protection Agency (EPA) (2004) identified agriculture as the greatest threat to rivers and streams, although it is difficult to measure and regulate due to the intermittent nature of agricultural activity and rainfall, resulting in hard-to-predict nutrient flow (Sharpley et al., 1995).

Phosphorus sorbs strongly to clay surfaces and is usually not expected to leach into local waterways in quantities of any concern. When animal manure is used as fertilizer it has historically been applied to meet crop needs for N. Currently there are no economically-viable alternatives to land application of manure and there is a lack of alternative disposal locations (Pautler and Sims, 2000; Sims et al., 2002). The long-term

practice of applying poultry litter to fields on the Eastern Shore of Maryland has resulted in P applications far in excess of crop needs (Kleinman et al., 2011a). Recent laws in Maryland have put limits on manure applications (Maryland Department of Agriculture, 2012), forcing farmers to supplement N crop needs with artificial fertilizer.

The EPA (2010) reported that in places with significant control over point source pollution, non-point has become the greatest source of P in waterways. The phosphate laundry detergent ban, advancements in wastewater treatment and banning of phosphate release from industrial sources have allowed more attention to be focused on agriculture: a major non-point source (Gächter et al., 1998). Certain practices can aid in improving excessive nutrient release, such as reducing fertilizer loads, managing fields as point-source areas, and removal of nutrients from the system where possible (Carpenter et al., 1998). The effectiveness of these practices is stymied by legacy P from previous long-term applications of fertilizer and manure, which have been shown to produce chronic losses to drainage waters. It could require decades to reverse high levels of P (Kleinman et al., 2011a). Dissolved inorganic P has a disproportionately large impact on eutrophication (Kleinman et al., 2011a), likely due to the soil reaching its maximum capacity in P sorption, and releasing excess P into the soil solution.

The Delmarva Peninsula today produces an estimated 600 million birds annually (Kleinman et al., 2011a) and is considered to have one of the most concentrated poultry industries in the U.S. (Pautler and Sims, 2000). Poultry litter is a common source of fertilizer, as many farmers run large scale poultry houses in conjunction with cash crops such as corn. The inputs of P via feed and fertilizers are greater than the outputs in animal products and crops, resulting in a net surplus of P in fields (Sharpley et al., 1998). The

heavy use of poultry litter has contributed to excess of P in soils over the last 40 years (Kleinman et al., 2011a), resulting in P leaching via surface runoff or subsurface flow into drainage ditches and eventually the tributaries of the Chesapeake Bay. Indeed, animals such as poultry typically retain only 30% of P in feed, thus allowing the rest to be released to the environment (Sharpley et al., 2001). The addition of the enzyme phytase to poultry and swine diets can potentially decrease the amount of P released by 15-30% and has become common practice in the U.S. (Applegate et al., 2007).

A potential response to the leaching of excess P relates to the 1970 Clean Air Act administered by the EPA, which includes requirements to reduce the quantity of sulfur dioxide (SO_2) emitted into the atmosphere (Fialka, 1998). Specific legislation has required coal-fired plants to reduce emissions of SO_2, nitrogen oxides (NO_x) and mercury (Hg). In accordance with the Clean Air Interstate Rule of 2005, a scrubbing process is now used to prevent SO_2 emissions, resulting in a high-quality gypsum by-product, for which production is expected to increase (Norton, 2008). The wet scrubbing system entails exposing flue gas to a limestone slurry. The reaction between the two produces a calcium sulfite ($CaSO_3 \cdot 1/2H_2O$) by-product that is subjected to a forced oxidation process in order to produce calcium sulfate ($CaSO_4 \cdot 2H_2O$) (Álvarez-Ayuso et al., 2011; Buecker et al., 2011). The resulting slurry is dewatered to produce FGD gypsum (Álvarez-Ayuso et al., 2011). In general, wet-gas desulfurization removes greater than 90% of SO_2 from flue gas (Álvarez-Ayuso et al., 2006).

Although gypsum is a key material in the production of wallboard for construction, a substantial excess is anticipated due to the new regulations, requiring energy companies to send it to a landfill, or put it to better use. Relative to most industry

by-products, FGD gypsum tends to be homogenous, with the potential to be free and cost little to transport (Penn et al., 2007). FGD gypsum contains little in the way of trace elements and may be more cost-effective than commercial gypsum. Even so, variability does exist and the FGD gypsum should be tested for purity before it is applied to soil. Heavy metals such as B, Mo, As, and Se are of potential concern, necessitating categorization of FGD gypsum by suitability, such as for construction or agriculture (Punshon et al., 2001). As a result of the new regulations, an estimated 15-17 million tons of FGD will be produced, in addition to what can be absorbed by the construction industry. The cost and space limitations on landfills make an alternative use highly desired. Agriculture has the potential to use 80 million tons of FGD gypsum per year and its use could be mutually beneficial to both the energy and agriculture sectors (Ramsier and Norton, 2006).

In the flat plains of Delmarva, close to tributaries and open water, high water tables are the norm, creating a need for farmers to artificially drain their fields. Organized land drainage began in Delmarva in the late 1700s and was large-scale by the 20th century (Vadas et al., 2007). This research was performed in the context of a concurrent study concerning the use of gypsum curtains as a physical and chemical means to impede phosphorus leaching into drainage ditches that empty into local tributaries (Fig. 1). Gypsum has been known and used as an important soil amendment for years. Among its most popular applications is to improve soil structure and infiltration, especially in saline-sodic and sodic soils in which dispersion and crust sealing are prevalent (Wallace, 1994). Research on the effects of gypsum on infiltration in acidic Coastal Plain soils is relatively new. In order to maximize the proportion of

excess P that flows to the gypsum barrier, surface runoff (unfiltered flow) should be minimized and subsurface flow (filtered flow) of soluble P towards the curtains should be maximized.

The EPA and United States Department of Agriculture (USDA) published a joint strategy in 1999 for sustainable management of nutrients in animal feeding operations via inputs and outputs to be adopted nationally by 2009 (EPA/USDA, 1999). Previous targets to reduce P by 40% by 2000 attacked the most accessible sources of pollution, still leaving work to be done in regards to less obvious non-point sources of P (Kleinman et al., 2011a). In the Spring of 1998 well–publicized outbreaks of Pfiesteria were blamed for substantial fish kills in the tributaries of the Chesapeake Bay, raising concern from the Maryland General Assembly (Coale, 2000). The resultant Water Quality Improvement Act (WQIA) of 1998 offered both long and short term strategies for the problem (Coale, 2000). Among them was a call that required N & P based management plans for manured areas and fines for not abiding by them.

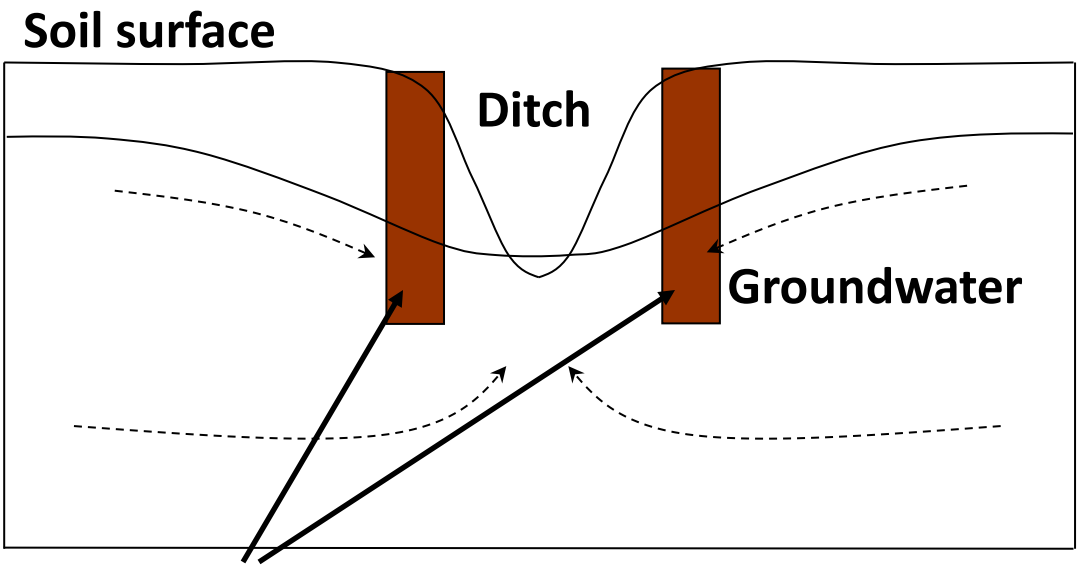


Figure 1. Arrows point to gypsum curtains, through which subsurface flow must pass before entering the ditch. Ideally, soluble P will precipitate with Ca in the curtain and not continue into the drainage ditch. Courtesy of Dr. Ray Bryant, USDA-ARS.

The WQIA also resulted in the Maryland Phosphorus Site Index as an evaluation tool in order to determine risk of P loss on a specific field site. Site specific-plans are necessary in order to engage in successful remediation (Carpenter et al., 1998), while minimizing adverse impacts on farm economies. The P-index is considered an important advance, in that it considers: soil P content, P application rate, method of application, and timing of application, as well as factors affecting transport of P (Sharpley et al., 2003). A form of the P-index now exists in nearly all states, including MD, although current models predicting P movement and its impacts do not consider legacy sources of P (Kleinman et al., 2011a).

Objectives

The main objective of this study was to assess the effect of shallow-incorporated FGD gypsum on infiltration rates through a poorly-drained Coastal Plain soil. It was expected that FGD gypsum application would increase infiltration rates on this soil. A secondary objective was to observe the effects of FGD gypsum on water-extractable phosphorus (WEP) levels in this same soil under identical treatment conditions. It was expected that FGD gypsum applications would significantly decrease WEP levels, indicating precipitation of P with available cations in the soil. A tertiary objective was to monitor any changes in sulfur concentrations at the study site. Should FGD gypsum add plant-available S to the effective rooting zone of major cash crops such as corn, it would provide immediate appeal as an economical soil amendment and best practice for local farmers. Many farmers in the region, including the owner of the current study site, currently include sulfur as part of their fertilization program to increase crop yield.

In addition to WEP, soils samples from the field were subjected to Mehlich 3 (M3) and ammonium oxalate extractions, and gradations of added soluble P in order to observe P sorption behavior. These data provided observations of possible changes due to FGD gypsum applications, as well as the opportunity to compare the relationships between the results of various P analysis tools and how these compare with what has already been established in the literature.

Expected Outcomes

The small amount of literature regarding the use of gypsum on Coastal Plain soils has indicated its utility beyond arid regions and dispersive soils. The results of this study have the potential to add a new best practice to the nutrient management arsenal for the Mid-Atlantic region. The expected increase in FGD gypsum supply could result in a win-win situation for both the local coal-powered energy industry and agriculture, assuming the economics of such a system are favorable for all parties.

On heavily manured soils with artificial drainage, WEP is of major concern for its potential role in eutrophication and will continue to be so for years to come due to legacy stores of P. FGD gypsum offers not only potential as a short and long-term agent to remediate excess soluble P, but also as a beneficial soil amendment for improved crop production. If the by-product demonstrates utility on any of the fronts investigated in this study, it would be welcome news for the local agriculture and ecology.

CHAPTER TWO: LITERATURE REVIEW

Ditches

The current study area on the Lower Eastern Shore of Maryland is within eyesight of open water ways, is flat, and has a seasonally high water table very close to the ground surface. In order to be productive farmland, it is common for fields here to be surrounded by drainage ditches in order to prevent soil saturation and allow equipment on the field earlier, while simultaneously providing a direct link to streams and rivers and encouraging subsurface flow in lieu of overland flow (Kleinman et al., 2007). The main goal of these ditches has been to direct water movement, without consideration to potential environmental risks, therefore allowing the transport of high levels of P from a variety of sources (Needelman et al., 2007) via subsurface water flow of P (Kleinman et al., 2007). In flat landscapes where there is a shallow water table, subsurface flow potentially contributes up to 90% of the P found in ditches (Kleinman et al., 2011a). However, it is important to note that even in a flat landscape on the Lower Eastern Shore, 34% of P in ditches has been found to be sediment-bound run-off (Kleinman et al., 2007).

Gypsum

Ramsier and Norton (2006) noted four potential uses for the FGD gypsum expected to flood the market following the mass installation of coal scrubbers: a fertilizer providing calcium (Ca) and S, a conditioner for saline/sodic soils to counteract maladaptive farming practices, an alternative source of electrolytes to prevent soil crusting, and a detoxifier of soils with excess exchangeable Al. The above recommendations are not directly related to the soil and climatic conditions of the current study area, but given the potential availability of FGD gypsum, researching the benefits the can be acquired on the Coastal Plain soils of the Delmarva Peninsula is worthwhile. As of 2011, only about 47% of FGD gypsum was being re-used (American Coal Ash Association, 2012).

Gypsum from other sources has been used as a soil amendment for many years. There is literature on the effects of mined gypsum, phosphogypsum (PG), and analytical grade gypsum used either in field or laboratory settings. Up to the present, however, the extent of research on FGD gypsum has been small due to its limited availability (Rhoton and McChesney, 2011). Use of FGD gypsum has also been limited due to unknowns about its environmental effects, including Hg release. Cheng et al. (2012) found that Hg concentration in soils was correlated with the amount of FGD applied and that the process used to produce the gypsum is important to its resulting quality. A study by Punshon et al. (2001) found that although FGD gypsum elevated levels of some heavy-metals in soil, it did not produce any symptoms of toxicity in plants. In order to avoid potential problems, they recommended limits be maintained on how much FGD gypsum

is applied. Any FGD-sourced gypsum should undergo chemical analysis before being applied to soils.

The longevity of gypsum effects after application is not well-known, but seasonal application could be beneficial to soils (Miller, 1987). If the anticipated surplus of FGD gypsum manifests, the supply should be available to make repeated applications possible.

FGD gypsum has the potential to offer beneficial effects to soil without being detrimental to crops (Stout et al., 1999). Punshon et al. (2001) found that low-grade FGD gypsum was neither a help nor a hindrance to early plant establishment on an acidic sandy soil in South Carolina, although there was a significant increase in biomass of corn, cotton, soybean, and radish plant after ten weeks of growth. These results suggest that the input of sulfates into the soil system may have benefited growth.

Rhoton and McChesney (2011) measured a significant increase in sulfur uptake among cotton plants on a silt loam in Mississippi and found that within a year Ca and S can be transported to 20-30 cm soil depths. The silt loam showed an average increase in soil Ca of 24% in the top 10 cm following three successive FGD gypsum applications, topping out at 29% in the 6.7 Mg ha^{-1} treatment, with little change at lower depths. There are data showing that surface application of gypsum will increase total S in the year that it is applied (Islam et al., 2012).

The literature on the effects of gypsum on pH reveals a variety of scenarios. Callahan et al. (2002) tested by-product gypsum on four different Northeast soils that were traditionally fertilized with manure and found that some soils increased slightly in pH while others decreased slightly. They attributed this change not to the gypsum itself, but the inevitable impurities to be found in a by-product, such as calcium carbonate

($CaCO_3$). Alternatively, Johnson et al. (2011) found that FGD gypsum application on a Coastal Plain soil (similar to the current study site) either significantly lowered soil pH or had no effect at all, attributing it to replacement of Fe and Al on colloidal exchange sites. A slight decrease in pH was noted by Favaretto et al. (2012), but only at the 2.5 cm depth, also attributing it to the displacement of Al^{3+} and H^{+} by Ca^{2+}. Murphy and Stevens (2010) noted slight decreases in pH on acidic soil in Ireland, noting that in addition to the displacement of Al^{3+} and H^{+}, SO_4^{2-} likely replaced OH^{-}, resulting in a net neutral effect on soil pH. They contend that in high Al soil, the acidifying effect mentioned above may predominate. Punshon et al. (2001) found no significant effect of gypsum on pH. It is assumed that although FGD gypsum has the potential to raise pH, it is not by much and will depend on the composition of the by-product used (Clark et al., 2001).

Gypsum and Infiltration

Much of the research testing the effects of gypsum as a soil amendment focuses on addressing dispersion, out of concern for maintaining high enough permeability to rainfall for salinity control and water storage in saline-sodic or sodic soils (Keren et al., 1983). The diffuse double layer theory proposes that soil solution near a negatively charged clay surface will predominantly contain positively-charged cations rather than anions. The character of these cations will largely determine the stability of soil structure. Monovalent sodium (Na) cations (present in excess in sodic soils), and with a large hydrated radius, will allow for a wider diffuse layer between clay surfaces, while higher-valence cations with smaller hydrated radii, such as divalent Ca, will more effectively hold clay surfaces together, thus strengthening soil structure (Bohn et al., 1985). Lebron et al. (2002) found that gypsum increased saturated hydraulic conductivity (K_{sat}) in columns packed with saline-sodic soil. Micrographs of the thin sections from the columns also showed a change in the shapes of aggregates following gypsum application. Furthermore, gypsum increased soil physical conditions, flocculation, and infiltration rate due to the addition of electrolytes. Subsequent reduction in exchangeable sodium percentage (ESP), due to chemical processes promoted by gypsum, was associated with larger soil aggregates.

A study by Keren and Shainburg (1981) found that the effects of gypsum lasted throughout a simulated rainy season in a lab setting using sodic soils. Water-content was higher in gypsum-treated soils and there was a correlation between the rain intake and moisture content of the soils. Significant effects were found by type (analytic, fertilizer by-product, mined), application rate, and the fragment size of gypsum. Even the lowest

application rate of 1.38 Mg ha^{-1} resulted in higher infiltration rates than the control. Industrial gypsum was more effective at maintaining higher infiltration rates than mined gypsum (7.5 mm $h^{-1}$and 5.5 mm hr^{-1}, respectively).

Ben-Hur et al. (1992) found that 5 Mg ha^{-1} of PG resulted in a decrease in soil loss, increased FIR values, and increased cumulative rainfall infiltration in a rain simulator study using surface applied PG on dispersive soils with low exchangeable sodium percentage (ESP) values. PG treatments prevented clay dispersion by what they determined to be the addition of electrolytes.

Tang et al. (2006) found that PG treated soils showed a decrease in soil loss, an increase in FIR and a decrease in cumulative runoff over all ESP levels (<2%, 5%, 10%, and 20%). The effect on infiltration rates showed greater efficiency at higher ESPs. They also found that these effects were amplified when used in conjunction with synthetic organic polymers (PAM).

In a lab study on silt loam loess and sandy clay with low ESP values, gypsum at rates of 2 and 4 Mg ha^{-1} significantly reduced runoff and reduced soil loss. Additionally, effects were stronger on the sandy clay, with a higher FIR and a slower drop in IR over time than the loess soil. On average, the FIR increased by 50%, and 100% for the 2 and 4 Mg ha^{-1} treatments, respectively (Yu et al., 2003).

Keren et al. (1983) found that relatively low gypsum application can prevent dispersal and clay runoff. Five Mg ha^{-1} applications of gypsum reduced yearly runoff regardless of ESP level and that surface application was better than incorporation to 10 cm in field studies. The electrolyte concentration when surface-applied was 10 times that of soil in which the same amount of gypsum was dispersed throughout a 10-cm depth.

They showed gypsum to be more effective at preventing erosion in soils with lower ESP. The Coastal Plain soils of the Delmarva Peninsula tend to have very low ESP values due to humid, wet conditions that are not conducive to build up of Na that occurs in arid regions.

Miller et al. (1987) performed a rainfall simulation study with a 5 Mg ha^{-1} application rate of PG on dispersive sandy loam Ultisols with low organic matter (OM) and found that it doubled the amount of water intake into soil and was especially effective in the soils with finer textures, in contrast to control surfaces that slaked and were compacted by rainfall. Additionally, PG delayed initiation of runoff and increased infiltration. Infiltration rates in the PG-treated soils remained higher until the end of the experiment.

Warrington et al. (1989) found that micro-reliefs of untreated soil samples subject to dispersion and sealing were visibly smoother, while those treated with PG showed roughness that correlated with decreased overland flow due to dispersion prevention resulting from added electrolytes. With an increase in slope, compared to the control, FIR of the PG-treated soil was higher and infiltration rate (IR) of PG-treatments decreased much less rapidly. Additionally, in soil samples with slopes of 5%-25%, soil losses due to rainfall were increased by 700% among control, but by only 200% in PG treatments. PG treatments decreased runoff at 5% slopes from 65% down to 32%. At a slope of 25%, 65% runoff was decreased to 23%.

Curtailing overland flow, or runoff, is a potential remediation to prevent nutrient loss of P (Kleinman et al., 2007). Runoff refers to rainfall that interacts with the surface soil before leaving the field at a depth of 1-5 cm (Sharpley et al., 2001). In cases where

the mass of P surpasses the sorption capacity of the soil, shifting the P flow path under the surface, via higher infiltration, may only redirect the problem, rather than solving it. Kleinman et al. (2007) found that annual flow (both overland and subsurface) and precipitation were related; moreover that 60% of total flow into ditches is from storms and a total of 58% of P losses were associated with storm events. Dissolved reactive phosphorus (DRP) concentration and annual flow were strongly related, signifying that more sources of soluble P are made active during wet years.

Phosphorus

Initial P guidelines were created to address crop needs, not water quality (Sharpley et al., 2003). Phosphorus runoff was not anticipated to be a problem due to its high sorption capacity in soils, resulting in no regulatory standard for groundwater dissolved P concentrations. Generally, the concentration of P on soil particles tends to be several orders of magnitude larger than in solution (Kleinman et al., 2011a). Alternative circumstances have evolved, however, on the Lower Eastern Shore of Maryland, where cultivation of crops and poultry production commonly run in tandem and agricultural land is subject to regular applications of animal manure. A study done on the Delmarva Peninsula (inclusive of the Lower Eastern Shore) by Kleinman et al. (2007), found a farm fertilized by poultry litter for 20 years had a M3-P content far beyond minimum values of environmental concern. M3-P alone cannot be directly tied to environmental risk because these tests were created only to address crop use. Excess P levels must be assessed in conjunction with potential runoff and subsurface flow parameters under diverse field conditions (Sharpley et al., 2001), if one is to have a reasonable assessment of potential effects on water quality.

Surplus of phosphorus as a result of long-term application of manure is among the most difficult nutrient management challenges (Kleinman et al., 2011a). P solubility varies across manure types and treatments (Sharply et al., 2003). Additionally, both timing and location of the manure-spreading affect soluble P transport (Walter et al., 2001). However, if there has not been a recent application of manure, soil test phosphorus (STP) may be helpful in making more stable predictions of potential P loss to water systems over time (Sharpley et al., 2003).

Soils have a strong affinity for P, but since most P is added to the soil surface, concern for P entering into water systems has traditionally been geared towards surface runoff. Downward transport should also be of concern, especially in soils with artificial drainage such as those on the Lower Eastern Shore. Vadas et al. (2007) showed a strong relationship between the average M3-P content from 0-75 cm soil depths and groundwater P concentration. Artificial drainage in a typically wet soil will accelerate transport of soil water and associated contaminants out of the local system. They found that P in groundwater is relatively restricted, compared to readily soluble nitrates, but during storms P was mobilized, moved deeper into the soil profile and persisted at elevated levels for days to weeks.

Generally, total losses of applied P in runoff are less than 10% of that applied, unless immediately followed by rain or on steep slopes (Sharpley et al., 2001). The ability to predict storms can offer some indication of potential P loss, especially in regards to runoff (Kleinman et al., 2011a). In terms of run-off potential, particulate P is usually the focus of concern, although the majority of P runoff in soils recently receiving surface application of poultry litter was found to be in the dissolved form in laboratory studies and pastured fields (Kleinman et al., 2011b). Water extractable phosphorus (WEP) is therefore a good indicator of dissolved P under these conditions (Kleinman et al., 2011b). If manure is incorporated into the soil upon application, the proportion of dissolved P drops substantially (Kleinman et al., 2011b). Sharpley et al. (2001) found that the concentration of dissolved P in subsurface flow increased as M3-P increased, validating the use of the M3 extraction as a predictor for P leaching via subsurface flow, rather than just an agronomic tool.

USDA-NRCS code 590 (U.S. Department of Agriculture-Natural Resource and Conservation Service, 2012), meant to establish a nutrient management standard, provides three options to identify if there is a need for P management: use of an agronomic soil test, threshold P values and a phosphorus site index (Sims et al., 2002). Agronomic soil tests, such as the M3 extraction, were not designed to address environmental problems, but because they are already widely used is soil testing labs across the United States, it is to our advantage to have them available as a tool in assessing the need for nutrient management (Sims et al., 2002). Very strong linear relationships have been found between M3 and the more costly and time-consuming ammonium oxalate extractions for both Al and P, but less so for iron (Fe) (Sims et al., 2002; Maguire and Sims, 2002).

The degree of P saturation (DPS) has long been considered a reliable indication of potential P loss from a soil (Dou et al., 2007). DPS assumes that amorphous Al and Fe oxides are responsible for a generous portion of P sorption in soils and is typically calculated using an ammonium oxalate extraction (DPS_{ox}, Eq. 1) to relate P, Al, and Fe on a molar basis (mmol kg^{-1}). Dou et al. (2007) found, in a study comparing paired fields sites that have either received no manure applications or long-term manure applications, that the DPS values were 80-90% in manured and 11-33% in non-manured soils. Oft cited researchers in the Netherlands have indicated a DPS_{ox} value of 25% as a threshold for potential loss of P to ground water (Nair et al., 2004). Above this threshold, which is generally well above agronomical optimums for soil P, it is expected that the quantity of weakly-bound P will increase rapidly (Maguire and Sims, 2002). Since the soils used in the Dutch study are considered similar to those of the Mid-Atlantic region in question,

this threshold is considered by many to be valid on the Delmarva Peninsula. Indeed, the threshold value for excessive STP (Mehlich 1) was established by the University of Delaware to be 50 mg kg^{-1} was found to correlate well with 25% DPS_{ox} (Pautler and Sims, 2000). Sims et al. (2002) found a significant relationship between WEP and DPS_{ox} and that the values of WEP and DPS_{ox} associated with UD's agronomic critical value (where soil P is adequate and will not limit crop growth) of 50 mg kg^{-1} M3-P were 1.9 and 21.2%, respectively. They supported the 25% environmental threshold for DPS_{ox}. On the other hand, Maguire and Sims (2002) found that a DPS_{ox} value of 56% was a valid threshold to indicate rapidly increasing loss of P in the Mid-Atlantic region. Additionally, they believed that the M3 phosphorus saturation ratio (M3- PSR, Eq. 2) was better at predicting losses of P then DPS_{ox}.

$$DPSox\ \% = \frac{Pox}{\alpha\ (Alox+Feox)} * 100 \qquad \text{Equation 1}$$

$$PSR = \frac{M3P}{M3Al+M3Fe} \qquad \text{Equation 2}$$

The α value used in the DPS_{ox} equation is considered a saturation factor meant to provide a probable representation of the portion of Al and Fe oxides that are actually available for P sorption. Many studies arbitrarily set α at 0.5 based on the previously mentioned Dutch study, allowing for easy comparison with other research (Kleinman and Sharpley, 2007). Van der Zee and Riemsdijk (1988) found that an average alpha value for a topsoil to be approximately 0.48 after a 40 h P sorption experiment. Using 0.5, researchers are able to compare results from a variety of different studies (van der Zee and van Riemsdjik, 1988). Previous work in the Mid-Atlantic region found alpha values

between 0.4 and 0.6 for oxalate extractions (Sims et al., 2002). In acid sandy soils, the alpha has been known to range between 0.3 and 0.7. Soil properties and reaction time will affect the calculated α (Pautler and Sims, 2000; van der Zee and Riemsdjijk, 1988). Van der Zee and Riemsdijk (1988) found higher α values for subsoils than topsoils. Kleinman and Sharpley (2007) chose not to use alpha at all due to the arbitrary nature in which it is applied. They instead used phosphorus sorption saturation (P_{sat}) as a term to describe the proportion of sorbed P based on P sorption capacity in terms of Al and Fe, extracted by either M3 or ammonium oxalate (Eq. 3). They found that estimating Psat with M3 P, Al, and Fe was comparable to more time consuming and costly methods for understanding P behavior, such as capturing sorption data by fitting data to isotherm models or calculating DPS_{ox} on a large array of soils. They showed that $Psat_{M3}$ and $Psat_{ox}$ where highly correlated (r = 0.94).

$$P_{sat} = \frac{Sorbed\ P}{P\ sorption\ capacity} \qquad \text{Equation 3}$$

Sims et al. (2002) found DPS_{ox} to be significantly correlated with WEP (r=0.86) and a strong correlation between M3-P and oxalate extraction of P and Al (r = 0.71 and 0.85, respectively). They also found a linear relationship between M3-PSR and DPS_{ox} (r^2 = 0.92). In contrast to other the other studies cited, Nair et al. (2004) calculated a DPS for M3 extraction using α = 0.5, and found a linear relationship with DPS_{ox} (r^2 = 0.97). Sims et al. (2002) argued that there was no experimental evidence for using the α value with M3 data, preferring the M3-PSR.

Sorption isotherms are measured by adding a known concentration of solute to a soil and allowing time for equilibration. The amount of the solute remaining in solution is then measured and used to calculate the concentration that sorbed to the soil during the wait time. Sorption isotherms can provide an indication of P behavior in soils and with a standardized procedure can provide reproducible results by sorption modeling (Nair et al., 1984). Previously sorbed P can affect P release and retention, as can Ca, Al, and Fe components (Dou et al., 2007). In comparing similar soils that had or had not been subject to years of manure applications, Dou et al. (2007) found maximum P sorption (S_{max}) to be 2-8 times greater in manured soils. Additionally, they found that the Smax for P sorption in the manured soils was similar to the amount of P initially sorbed to the soil (as indicated by ammonium oxalate extraction of P).

The most popular of the isotherm models are the Langmuir (Eq. 4) and Freundlich models (Eq. 5), and various adaptions of the two. Many prefer the Langmuir due to its inclusion of a S_{max} component, which is of interest to those concerned with P loss from agricultural fields. Nair et al. (1984) found that the Freundlich model was better suited to sorption data than the Langmuir, based on data from twelve different soils, also noting that the Freundlich tended to deviate to a higher predicted P sorption.

The predominant flaw that it is often cited for the Langmuir model is that in order to perform the nonlinear regression needed for sorption data, it must be assumed that the independent variable (the x-axis variable) is error-free or that the error remains constant (Bolster, 2008; Bolster and Hornberger, 2007). This assumption cannot be made in regards to sorption data because the independent predictor variable is the equilibrium concentration of P (indicated by *C* in Eq. 4 and 5), which is experimentally-measured and

therefore subject to error, possibly providing biased results (Bolster, 2008; Tellinghuisen and Bolster, 2010). Bolster and Tellinghuisen (2010) found increasing errors in both the equilibrium concentration and sorbed concentration with increasing values of the two variables, when the variables were unweighted. However, Bolster (2008) compared Langmuir with two mathematically equivalent equations that addressed the error issue and did not find any significant differences in the estimated parameters among the soils studied. Choosing the incorrect model for sorption data can have serious implications in regards to the P index, as S_{max} may not provide a realistic reflection of the state of the soil and accuracy requires choosing the most appropriate model (Bolster and Hornberger, 2007).

Langmuir $S = \frac{SmaxKC}{1+KC}$ Equation 4

Freundlich $S = K_f C^n$ Equation 5

Where: S = sorbed P concentration (mg kg^{-1})

K = Langmuir binding-strength coefficient (L mg^{-1})

C = equilibrium concentration P (mg L^{-1})

S_{max} = maximum sorption capacity of the soil (mg kg^{-1})

K_f = Freundlich coefficient

n = Freundlich fitting parameter (aka. heterogeneity factor)

Other studies that attempted to address error issues by weighting the variable did not find conclusively that unweighted least squares regression would result in significant

errors in parameter estimation (Bolter and Tellinghuissen, 2010). Work by Tellinghuisen and Bolster (2010) found that with properly weighted least-squares analysis, however, that Freundlich was a better fit than the Langmuir equation 95% of the time and argued that if unweighted least squares is used, r^2 values may not be a good indication of how well the model fits.

Phosphorus and Gypsum

P-sorbing materials typically contain Al, Fe, Ca, or magnesium (Mg) (Penn et al., 2007). Although FGD gypsum is often found to be a relatively pure source, this is not always the case, resulting in variable chemical effects on aspects such as P-sorbing capacity (Johnson et al., 2011). Generally, Fe and Al in soils represent the most reactive portion of the soil matrix able to remove soluble P (Penn et al., 2007). In acidic soils, P-sorbers such as gypsum act as electrolytes, likely promoting P sorption via mass action release of Al and Fe from exchange sites, resulting in precipitation with P, or allowing for adsorbtion P onto mineral surfaces (Callahan et al., 2002). In order for Al to be an effective sorbing material for P, the pH needs to be less the 7.5. Ca and Mg become more effective at precipitating at pH 6-7.5 (Penn et al., 2007). Callahan et al. (2002) asserted that in a neutral soil of pH 7.1, calcium-phosphate would be the dominant P-sorption process.

Most studies looking at the use of gypsum to mediate P excesses concentrate on erosion and runoff, as leaching has been considered of lesser importance due to the strong sorption tendencies of P (Gächter et al., 1998). In soils with abnormally high P levels, it has become apparent that subsurface flow of P in soil solution is a real challenge. Key factors to be considered in choosing a P-sorbing material are the cost, potential contaminants, P-sorption characteristics, physical properties, and potential disposal needs in the future (Penn et al., 2007). It needs to be cheap, requiring minimal resources for transport and storage, and cannot be detrimental to crops (Callahan et al., 2002). $CaSO_4$ is better at P retention than calcium carbonate ($CaCO_3$) because of its higher solubility that promotes release of more Ca^{2+}, encouraging Ca-phosphate bonding and precipitation,

even in acidic soils (Penn et al., 2007; Murphy and Stevens, 2010), there may also be potential for competition for sorption sites between sulfates and phosphate (Borůvka and Rechcigl, 2003).

Johnson et al. (2011) found a variety of coal-combustion by-products were effective in reducing dissolved P by 32-55% in the 1st year after shallow-incorporation. Specifically, FGD gypsum showed significant results at the lowest application rate of 7.5 Mg ha^{-1}. In this Delmarva study they found that WEP in runoff was temporarily reduced, but particulate P was still available, thus runoff P was not significantly impacted and FGD would potentially be more useful where dissolved P is the primary form of P targeted. There was a decline in the effectiveness of shallow-incorporated FGD after the first year and no significant difference between treatments in the third year after application, except in the highest treatment at 30 Mg ha^{-1}.

Callahan et al. (2002) found several rates (ranging from 6.5-52 Mg ha^{-1}) of by-product gypsum to be effective at P sorption, and that decreases in WEP and M3-P concentrations remained stable from 21 days until the end of the experiment (120 days) in lab-induced incubations with P-rich loamy soils (pH 5.5- 7.1). They suggested this was because the sorption process occurred rapidly and then remained stable over time.

Stout et al. (1999) found FGD reduced water soluble phosphorus concentrations in shale-derived silt loams from PA. The effect was greatest up to 7.5 Mg ha^{-1} and diminished beyond this application rate. Water-soluble P was decreased by 50%, but FGD application did not reduce M-3 P below what is needed for plants growth. Murphy and Stevens (2010) found gypsum application consistently decreased WEP anywhere from 14-56%, in acidic soils in Ireland (pH 5.3-6).

Sulfur

Tabatabai (1984) gave a succinct history of the evolution of sulfur fertilization. Starting in the 18th century, a period referred to as "Reign of Gypsum," gypsum was widely used as a fertilizer and, according to the author, its benefits were somewhat overestimated. By the mid-19th century and through the early turn of the century, gypsum itself was out of favor as the sulfur needs of plants were ignored and superphosphate was popularized. By the end of the 19th century, some scientists began to question the assumption that the natural supply of sulfur in soils was sufficient for crop needs and began researching the effects of sulfur fertilization on crops. Ironically, around mid-century, as acknowledgement of the importance of sulfur for plant health grew, high-analysis N and P fertilizers became popular. Because more traditional fertilizers like superphosphate and ammonium phosphate contained some amount of gypsum (12% and 24%, respectively), they supplied sulfur even if that was not the intent of their use. The high-analysis fertilizers were engineered to be far more pristine, and therefore lacking in substantive levels of S.

Sulfur is now known to be one of the sixteen nutrients essential for plant growth and an important component of amino acids required for protein synthesis (Brady and Weil, 2008a; Tabatabai, 1984). It is the fourth most important nutrient after N, P, and K and generally speaking, it is believed that agronomic crops need S in amounts similar to P (Khan et al., 2006; Tabatabai, 1984). As S and N are closely associated in protein synthesis, S requirements will vary with the supply of N needed for a crop. Due to the tandem nature of these two nutrients, if S is the limiting factor for a plant, providing more N is not going to help its growth (Tabatabai, 1984). Indeed, in soybeans that responded

positively to S fertilization, stoichiometric relationships between N and S have been found more accurate in identifying S responsiveness than any single variable (Salvagiotti et al., 2012).

Sulfur deficiency has become a salient issue due to several factors: use of high-analysis fertilizers that contain little or no S, increased crop yields, decreased use of S as a pesticide, more intensive cropping, and a decrease in atmospheric S due to stiffening restrictions on emissions from coal-fired plants (Boye et al., 2010; Tabatabai, 1984). The latter factor prompted Tabatabai (1984) to advise taking the potential loss of atmospheric S into consideration when analyzing the costs and benefits of minimizing SO_2 emissions, arguing that where atmospheric S is very low, there would not be enough mineralization of organic sulfur to address crop requirements. Indeed, this prediction proved true, as S deficiencies are quite common today on the east coast of the U.S. (Smith, 2011; University of Delaware Extension, 2013). Of economic concern, S deficient conditions may reduce the efficiency of applied N, P_2O_5 and K_2O (Khan et al., 2006), resulting in releases of N and P to the environment, even though the crop may need these nutrients.

In humid regions that are not fertilized, most sulfur absorbed by plants comes from soil organic matter (SOM) and mineralization rates are not expected to change even in long-cropped soils, unless organic S sources are added to the soil (Eriksen, 2009). Organic S accounts for more than 95% of total S in temperate, humid and semi-humid regions, yet about 50% of that is considered highly labile (Tabatabai, 1984). In order for sulfur to be absorbed by plants, it must be converted to sulfate by microorganisms (Tabatabai, 1984). All fractions of soil organic S involve transformation processes and most S taken up by plants derives from the organic sulfur, even when mineral S in

supplied (Boye et al., 2010). Recently immobilized sulfur is more prone to mineralization than the bulk organic S in the soil (Ghani et al., 1993) and immobilization into more stable organic fractions in a relatively slow process (Eriksen, 1997). Because most S does derive from OM, there is some belief among agronomists that a soil with at least 3% OM probably need not worry about S fertilizer (Smith, 2011). Spring increases in microbial activity, incited by high amounts of OM and warmer temperatures, will temporarily result in net immobilization of S as sulfates are incorporated into microbial tissue. Sulfur availability can also be stifled when C:S ratios reach above 400:1 (Brady and Weil, 2008a). Due to these complexities in S availability, measuring total S for crop purposes, rather than only sulfates, better predicts available stores of S that may become plant-available via transformations over time (Ketterings et al., 2011).

Islam et al. (2012) found that both 15 and 30 kg ha^{-1} of S, provided in the form of gypsum, had significant effects on soil S status after crop harvest, but found a significant reduction in soil available P. They indicated that this trend had been observed in other common crops, but did not make mention of why this occurred. Because their research was completed on soil with a relatively high pH value of 7.7, it seems likely that the Ca provided by the gypsum precipitated with P, to form calcium phosphate (Callahan et al., 2002; Penn et al., 2007).

Salvagiotti et al. (2012) found that light soils, with low OM and those that have suffered erosion were most responsive to application of gypsum for fertility purposes. Application of gypsum has also resulted in an increase in S in the soil post-harvest and improved N uptake in chickpea, although the amount of N absorbed depended on the level of S applied to the soil (Islam et al., 2012).

Summary

Agriculture is now considered the primary source of N and P nutrient excess entering the Chesapeake Bay (EPA, 2010). The nature of the Lower Eastern Shore of Maryland, with its high water table, expansive network of both public and private drainage ditches, and intense agricultural output requires special attention in the effort to curb nutrient loss. The ditch system has the potential to fast-track nutrients to connecting waterways, and farmers who live and work in this part of the United States are subject to increasing regulations in regards to land management.

The potential of FGD gypsum as a beneficial soil amendment is growing as production increases and becomes cleaner. I found no evidence of negative effects on plant growth, and the presence of heavy metals in today's FGD gypsum product is small enough not to raise concerns about toxicity. The literature reviewed does not provide evidence of a specific effect of FGD gypsum on pH. It is preferable not to add anything to the acidic soils of the Lower Eastern Shore that would further decrease pH and therefore render nutrients unavailable to crops.

There is a wealth of research on the positive effects of gypsum on soil structure and infiltration in saline-sodic soils, attributable to changes in soil chemistry provided by the gypsum. The effects of gypsum on Coastal Plain soils have been less researched, but due to the steadily increasing supply and the pressure to address the issue of nutrient management, it is important to collect as much information as possible. The ability of gypsum to affect infiltration on such soils is debatable, because there has been little work in this area. Hopefully, this research can shed more light on the benefits, or lack thereof, that FGD gypsum can provide in the soils of the temperate Maryland climate.

Among the biggest challenges facing regulators on the Delmarva Peninsula is how to accurately predict P losses from agricultural fields and effectively mediate the problem by providing accessible, accurate, and just assessments to farmers. The best way to meet this challenge would be to use a protocol already in place at regional labs for recommending seasonal fertility plans. Using the familiar soil tests to make reliable environmental assessments would help to stream-line nutrient management planning. There is accruing evidence that common STP extractions and water extractions can provide the necessary means for reliable environmental assessments. This research is meant to be additive to this information set.

Research on the beneficial use of FGD gypsum as a remediation tool to control P loss from fields is steadily growing at a time when the urgency to limit excess P in waterways is great. Much of this research involves using FGD gypsum as a filter in or near drainage ditches to render P insoluble by precipitation with Ca (McGrath, 2013). There is not as much information available on how FGD gypsum impacts P loss when directly applied to land. An added benefit of land application is the addition of S to the soil. Ironically, current the air-quality regulations that have resulted in the production of by-product FGD gypsum are also linked to growing reports of S deficiencies. Direct application of FGD gypsum to soil shows promise in providing additional stocks of S for eventual plant uptake.

CHAPTER THREE: METHODS AND MATERIALS

Field Study

Location

A field study was conducted on the Coastal Plain of Maryland in Somerset County, just north of Crisfield, MD (Fig. 2). The field under study is 4.53 ha (11.2 ac), flat, and has an annual high water table naturally at or near ground level, requiring artificial drainage in order to be suitable for crop production. Drainage ditches exist all along the perimeter of the field. This field was subject to fertilization with poultry manure, produced on-site or purchased, for several decades before stricter regulations impeded its use.

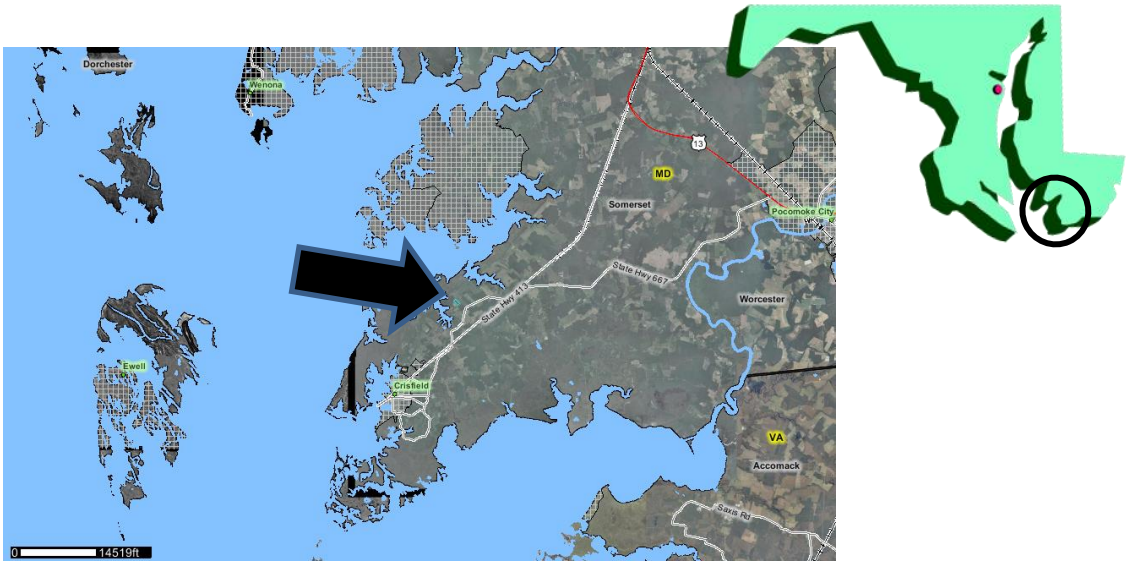


Figure 2. Location of field site on the Lower Eastern Shore of MD, near the town of Crisfield. There is a water body within eye sight when standing in the field.

Figure 3. White border indicates the perimeter of the study site, location of drainage ditches, and gypsum curtains. Dashed yellow lines are approximate locations of treatment rows. Lower case letters indicate approximate location of infiltrometers: a, b, c, d for each treatment level.

Field Infiltration

In January 2012, FGD gypsum was surface-applied by a manure spreader and shallow-incorporated to a 5-cm depth in parallel rows according to four treatment levels: 0, 5, 10, and 15 Mg ha^{-1}. Each row was approximately 400 m long and 13 m wide (Fig. 3). Measurement of infiltration rates began in March 2012 using a constant-head double ring infiltrometer. The double ring infiltrometer allows for less complicated measurement and calculation of infiltration by limiting measurement to only vertical water infiltration. The rings were driven into the ground to a 10-cm depth. Surface vegetation was left in place to simulate natural field conditions and care was taken to place the inner ring away from recent crop rooting zones that could potentially skew infiltration data due to root channels.

Each of the two rings was filled with water to equivalent heights. A Mariotte tube supplied water through a siphon in order to maintain the ponded water at a constant head above the ground surface in the inner ring (Fig. 4). The water level in the outer ring was monitored to manually maintain the same height. Over the course of several hours, water loss from the Mariotte tube was recorded at various time intervals. When the rate of water loss per unit time at successive readings became steady, the run was suspended and the final readings were considered the FIR. Three to six hours were required for the rate of infiltration to approach a steady state. Four infiltrometers were set up at evenly-space intervals (a-d, Fig. 3) within each treatment row, for a total of 16 infiltrometer sites. Infiltrometer readings at each site were taken pre-planting and post-harvest in March 2012 (i.e. two months post-application), November 2012 (i.e. 10 months post-application), and May 2013 (i.e. 16 months post-application). Data was not collected in the fall of 2013 due to compromising field management practices. There were no additional applications of FGD gypsum after January 2012.

Figure 4. Double-ring infiltrometer for measuring infiltration rate set up in the field. The Mariotte tube in the background feeds water into the inner ring in order to maintain a constant water head. A measuring tape affixed to the side of the Mariotte tube allows monitoring of the volume of water infiltrating into the soil.

Questions arose in regards to the accuracy of FGD gypsum application to the treatment rows. Therefore, analysis and results were considered by treatment level as well as by exchangeable Ca^{2+} as a gypsum surrogate (Porta, 1998). Although the Ca cations may not derive exclusively from FGD gypsum, relative levels should suffice to correlate ion concentration to infiltration behavior. Starting with the November 2012 field work, five soil samples to an approximate depth of 15-20 cm were pulled from the area within the perimeter of the inner ring immediately following collection of infiltration data.

Raw infiltration data from the field was inserted into the Philip infiltration equation (Eq. 6) in order to obtain parameters to be used in analysis. The Philip equation is physically-based (Mbagwu, 1994) and provides a fair estimate of K_{sat} for long-term precipitation. Transmissivity (A) refers to the ability of the soil to transmit water under the influence of gravity and is comparable to K_{sat}. The derivative (Eq. 7) may be used to model infiltration rate (*i*) on long-term precipitation. The Philip equation works better than some alternative models to predict vertical flows (Hillel, 2004).

$$I(t) = St^{1/2} + At \qquad \text{Equation 6}$$

$$i = \frac{1}{2}St^{-\frac{1}{2}} + A \qquad \text{Equation 7}$$

Where: I = cumulative infiltration

t = time

S = sorptivity

A = transmissivity

i = infiltration rate

Shallow soil columns were retrieved from the field site in June 2013. A 7.62 cm wide by 7.62 cm deep (3 in x 3 in) steel ring was driven into the ground with a drop hammer, extracted and excess soil was removed. Sixteen samples were retrieved: one for each infiltrometer location. It turned out that several weeks before this work, the owner of the property land-leveled the field in order to address an issue of variable ponding. In the lab, the bottom of each core was covered with cheesecloth and saturated from the bottom overnight. Each was then set on a stand that allowed water to exit the bottom into a

graduated cylinder while being fed water from the top to form a constant head (Fig. 5). Similar to the infiltrometer method described above, the volume of water collected in the graduated cylinder was measured per unit time until a constant rate was assured. Darcy's Equation (Eq. 8 and 9) was applied to acquire a K_{sat} value and converted to mm h^{-1}. After obtaining a K_{sat} value, each core was oven-dried at 105° C for 24 hours to obtain bulk density values in g cm^{-3}.

$$q = \frac{Q}{A \cdot t} \qquad \text{Equation 8}$$

$$K_{sat} = q \cdot \frac{\Delta z}{\Delta h} \qquad \text{Equation 9}$$

Where: q = Darcy velocity (cm sec^{-1})

Q = outflow of water (cm^3)

A = cross sectional area of the soil column (cm^2)

t = sec

Δz = height of soil column (cm)

Δh = height from constant head to free water (cm)

Soil Sampling and Chemical Analysis

According to the USDA/NRCS soil survey, the soil here is predominantly Othello, Quindocqua, or a complex of Othello/Fallsington (Table 2). However, the scale of the field is too small to be confident in the delineations obtained from the web soil survey.

Figure 5. Set- up for saturated conductivity (Ksat) experiment. Soil columns receive water from the trough in the background to maintain a constant head above the column. Water leaches out of the soil into the graduated cylinders below. Volume of water is measured per unit time.

Table 2. USDA-NRCS Soil Survey Data. The scale of the map is too small to accurately describe the study site, but is representative of soils in the region.

Map Unit Symbol	Map Unit Name	Acres	Percent Area
OoA	Othello silt loam, loamy substratum, 0 to 2 slopes	2.5	22.0%
OvA	Othello-Fallingston complex, 0 to 2 percent slopes	3.3	29.9%
QuA	Quindocqua silt loam, 0 to 2 percent slopes	5.4	48%
Totals for Area of Interest		11.2	100.0%

Soil Series	Taxonomic Class
Othello	Fine-silty, mixed, active, mesic Typic Endoaquults
Fallinsington	Fine-loamy, mixed, active, mesic Typic Endoaquults
Quindocqua	Fine-loamy, mixed, active, mesic Typic Endoaquults

Four 1 ¾" diameter cores were taken around each infiltrometer site. Three of the cores were approximately a meter (1.04 m), one extended to a depth of approximately two meters (2.08 m), resulting in 48 one-meter cores and 16 two-meter cores. Cores were split in half lengthwise; one half used for taxonomic classification, the other was used for chemical analysis of total S at depths of approximately 15, 30, 61, and 91 cm (6,12, 24, and 36 in, respectively), performed at the University of Delaware Soils Testing Program (UDSTP; EPA3051/EPA3050B). Typical maximum root depths for corn and soybean in a loam soil are 90 cm and 74 cm, respectively (Dwyer et al., 1988). Ketterings et al. (2011) reported that total S better predicts available stores of S as some portion of it may become plant-available via transformations over time.

Several separate soil sampling events occurred in this study (Table 3). The earliest sampling (Set A) was of ten 20-cm soil cores forming a transect along the length of the research field in January 2012, providing baseline information for soils in the field. In November 2012, approximately ten months after initial FGD gypsum application, five 20-cm soil samples were retrieved from each double-ring infiltrometer site immediately after measuring infiltration. Each set of five samples were mixed into a composite, for a total of sixteen samples (Set B). The same procedure was done in March 2013 and May 2013 (Sets D and E). No samples were taken in the fall of 2013 due to alterations to the research area. An additional set of 20-cm soil samples were taken in January 2013 along transects in each treatment row, ten samples per treatment, resulting in forty total samples (Set C).

Samples sets B, D, and E were tested for pH using an Accumet AB15 Basic pH meter. Samples were air-dried and sieved to passed through a 2-mm sieve. Ten grams of

each sample were added to 10 mL of deionized (DI) water and were stirred with a glass rod to create a homogenous slurry. Each samples was then left to equilibrate for 15 min, stirred again, equilibrated for an additional 15 min, stirred and measured with a potassium chloride-filled combination glass electrode. Electrical conductivity (EC, dS m^{-1}) was measured in the field by inserting a portable soil EC meter (Oakton ECTestr11+) into a paste of soil and DI water. Total Ca was measured at UDSTP (EPA3051/EPA3050B) on sets B and E.

WEP is considered the best indicator of dissolved P in fields recently receiving manure (Kleinman et al., 2011b), as it is indicative of P available for transport through ground water. Circumstances resulting from multiple project partners, financial allocations, and scheduling restrictions resulted in WEP extraction being performed at three different labs: UDSTP (Sets A, B, E), USDA-ARS University Park, PA (Set C), and the University of Maryland College Park (UMCP) Ag and Environmental Studies Lab (Sets B, D, E). At the UMCP lab, air-dried soil was passed through a 2 mm sieve. For each sample, 2 grams of the soil and 20 mL DI water were placed in a reciprocating shaker for one hour and then centrifuged at 2000 rpm for 15 minutes. Using a Millipore filtration apparatus and 0.45 µm filters, the resulting supernatant liquid was filtered and analyzed for P.

Water extracted P solution can be analyzed using either inductively coupled argon plasma spectrometry (ICP) or colorimetry. There is some controversy in regards to which is a better measurement, although ICP may provide a more accurate measurement of WEP in manure (Wolf et al., 2005). Pierzynski et al. (SERA-17) found that ICP and colorimetric analysis were well correlated in samples with high levels of P, although Self-

Davis et al. (2009) recommends using ICP analysis for WEP. In this study, extracted solutions were measured by ICP at the UDSTP and USDA-ARS labs, and by colormetric analysis with a Lachet QuikChem 8500 Flow Injection Analysis System, Method 12-115-01-1-A (Hach Company, Loveland, CO) at the UMCP lab.

Table 3. Soil sampling schedule. Soil sets retrieved from the study site in chronological order.

Date	Set A	Set B	Set C	Set D	Set E
Jan 2012	Transect of 10 samples				
Nov 2012		One composite sample per infiltrometer site			
Jan 2013			Transect 10 samples /per treatment row		
Mar 2013				One composite sample per infiltrometer site	
May 2013					One composite sample per infiltrometer site

Sets B, D, and E can be directly linked to infiltration measurements. Sets A and C provide general representative soil samples from the field and treatment rows.

Ammonium oxalate extractions were performed on Sets B, D, and E at UMCP. Soil was air-dried and passed through a 2-mm sieve. Forty-mL of ammonium oxalate/oxalic acid ($(NH_4)_2C_2O_4AH_2O + H_2C_2O_4A_2H_2O$) extracting solution was added to 1.00 g of the soil in centrifuge tubes. The tubes were wrapped in aluminum foil in order to allow the reaction to occur in the dark (McKeague and Day, 1966). They were then laid horizontally on a reciprocating shaker for two hours and centrifuged at 2000 rpm for thirteen minutes. The supernatant liquid was filtered through Whatman #42 filter paper

and sent to the Agricultural Analytical Service Lab at Penn State University (PSU) for ICP analysis.

P sorption isotherms were fitted to Sets B, D, and E. Thirty mL of 0, 0.1, 1, 5, 10, 25, 50, or 100 mg P mL^{-1} solution were added to tubes that contained 2.00 g of air-dried soil, sieved through a 2-mm screen. The tubes were laid horizontally in a reciprocating shaker for twenty-four hours, followed by thirteen minutes in a centrifuge at 2000 rpm. The supernatant liquid was then filtered through a Millipore filtration apparatus with a 0.45 µm filter and analyzed for P by the molybdate blue method on a Lachet QuikChem 8500 Flow Injection Analysis System, Method 12-115-01-1-A (Hach Company, Loveland, CO). Measured *C* (equilibrium P concentration in mg L^{-1}) was subtracted from the initial amount of added P in order to calculate *S* (sorbed P). Both data points were fitted in a non-linear regression in order to obtain parameters *K* and S_{max} (Eq. 4).

Alpha values (Eq. 10) for DPS_{ox} were calculated by the equation below where S_{max} is the maximum P sorption potential, as predicted by the Langmuir equation.

$$\propto = \frac{P_{ox}+S_{max}}{Al_{ox}+Fe_{ox}} \qquad \text{Equation 10}$$

M3 extraction and analysis was performed at UDSTP (Set A), USDA-ARS (Set C) and at UMCP (Set B, D, E). At UMCP, twenty-five mL of M3 extracting solution (0.2 N CH_3COOH + 0.25 N NH_4NO_3 + 0.015 N NH_4F + 0.013 N HNO_3 + 0.001 M EDTA) (Mehlich, 1984) was added to 2.5 g of soil that had been air-dried and passed through a 2-mm sieve, and put on a reciprocating shaker for 5 minutes. The soil

suspensions were then immediately filtered through Whatman #41 filter paper. The filtered solution was then sent to PSU for ICP analysis.

FGD gypsum used in the field experiment was sourced from the Brandon Shores Generating station in Anne Arundel County, Maryland. Chemical analysis was performed by Phase Separation Science, Inc., on behalf of Constellation Energy Group. The full data set is not provided here for proprietary reasons. The percent composition for heavy metals was well within acceptable limits. Pure gypsum would be expected to have a neutral pH of 7; the batch applied in January 2012 had a pH of 6.4. Select information from the analysis is used in this paper only to further discussion.

Rainfall Simulation

Location

A laboratory-based simulation of the field experiment was conducted in a facility at the USDA's Beltsville Agricultural Research Center (BARC) in Beltsville, MD. Soil used for the study was retrieved from an area of the farm in Crisfield immediately adjacent to the field study location. The soil is similar in origin, but differs in its recent usage, having been left fallow for several decades. Therefore, it has not been subject to the effects of cultivation, tillage practices, or manure application.

Simulated Rainfall

Soil was air-dried and manually crushed through a 4.75 mm sieve, then packed into a 20 x 40 x 16 cm metal tray above 9 cm of sand. The soil was packed to a depth of 5 cm at a bulk density of 1.5 g cm^{-3} (typical for the study field). The trays were perforated along the bottom and lined with cheesecloth to allow water to exit. In order to mimic the conditions of the field study, FGD gypsum was applied to trays at the same rates (0, 5, 10, 15 Mg ha^{-1}), as well as a 30 Mg ha^{-1} treatment. Treatments were mixed into the soil before packing, in part to mimic the shallow incorporation in the field and also to prevent surface sealing by the gypsum (Fig. 5). After packing, each surface was loosely covered with straw, to mimic the field experiment's surface vegetation. The trays were positioned at a 5% slope and were equipped with a spout that directed any runoff into a receptacle. The receptacle was retrieved approximately every five minutes in order to record volume (mL) of run-off for 90 min. Twenty-four hours later they were

subjected to another 60 min of rainfall. Infiltration rate was determined by subtracting runoff from total precipitation.

The rainfall simulator (Fig. 7) was built at the University of Maryland College Park campus, with specifications closely aligned with Meyer and Harmon (1979). It consisted of two oscillating 80150 Veejet nozzles set 3 m above the ground, approximately 2.5 m above the surface of the packed soil. Mean water drop diameter was 2.2 mm, with an impact energy of 275 kJ ha^{-1} mm^{-1} Precipitation rate was set at approximately 50 mm h^{-1}. The coefficient of variation was not ideal across the precipitation area (0.93, 0.91, 0.97 for the three tray positions), but was accounted for in calculating infiltration rates.

Statistical Analysis

Microsoft Excel 2010 was employed for all analysis. Much of the data in this paper is presented using only descriptive statistics because the primary assumptions required to make broader inferences were not met by the sampling technique used. The laboratory rainfall simulation was replicated and randomized, fulfilling required assumptions for using analysis of variance (ANOVA), also available and reliable in Excel. Wraith and Or (1998) promote the use of spreadsheet software as an alternative to costly and less available statistical software for nonlinear parameter estimation. The nonlinear optimization tool in Excel known as Solver can be easily and effectively used for fitting nonlinear data, such as infiltration and P sorption curves. Bolster and Hornberger (2007) showed that running isotherm models on SAS and Excel produced almost identical results in regards to the fitted parameter values, SSE, and standard error of parameter estimates. Therefore, Excel was used for modeling purposes. Solver

automatically runs a series of iterations to minimize SSE for best-fits of measured *C* and *S* data to a non-linear curve. Sorption data were fitted using an Excel spreadsheet provided for researchers by Carl Bolster of the United States Department of Agriculture-Agricultural Research Service (described in Bolster and Hornberger, 2007), which includes the formulas necessary to estimate Langmuir parameters *K* and S_{max}.

Figure 6. Packing soil trays for rainfall simulation. 20x40x16 cm dimensions with 9 cm of sand on the bottom (left) and 5 cm of soil on top (right). FGD gypsum treatments were mixed with soil before packing the trays. In the forefront is the trough that will collect runoff during the simulation (filled with newspaper in the image).

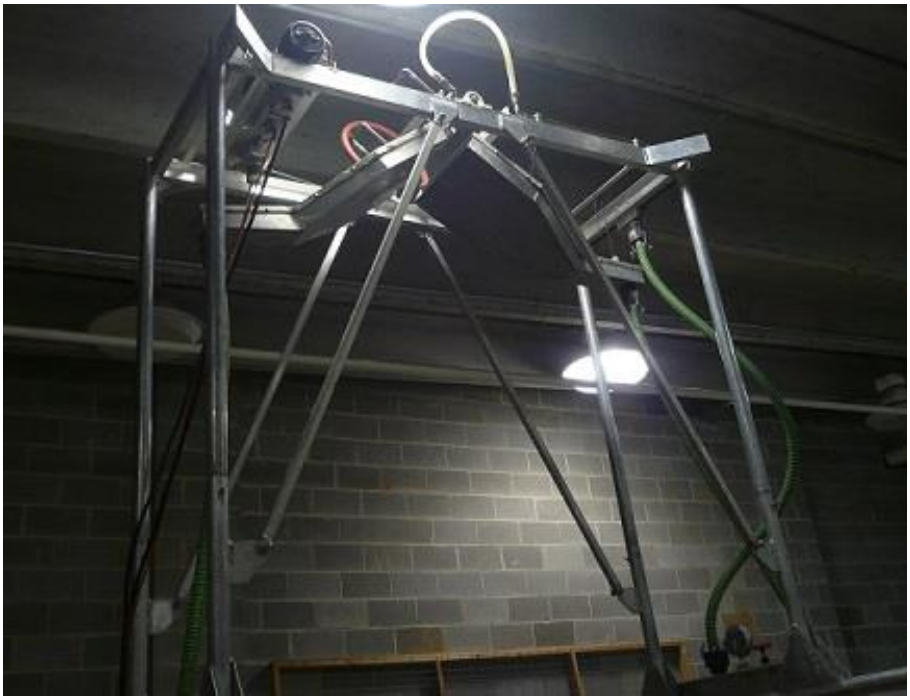


Figure 7. View of top to rainfall simulation apparatus. The hoses at the top connect to the two Veejet nozzles that oscillate back and forth to simulate rainfall at pre-programmed rate.

CHAPTER FOUR: RESULTS AND DISCUSSION

Soil Characterization

Initial testing of composite 20 cm depth soil samples along a lengthwise transect in January 2012 showed levels of M3-P in the 293 - 418 mg kg^{-1} range, consistent with other fields in the county under similar conditions. There were some fundamental differences in the field soils and the soils used for the rainfall simulation, based on soil tests run at the UDSTP (Table 4). Notably, the soil for the rainfall simulation, which had not been cultivated in several decades, differed from the adjacent field where the FGD gypsum treatment was applied. Lab analysis showed that substantially lower pH, OM, M3-P, base saturation, and P saturation ratio. It was used for the rainfall simulation because it was known not be contaminated by previous FGD gypsum applications.

Notably, FGD gypsum treatment had no significant effect on pH values (Fig 8), in accordance with published research (Callahan et al., 2002; Favaretto et al., 2012; Johnson et al., 2011; Murphy and Stevens, 2010; Punshon et al., 2001). EC increased with FGD gypsum, as expected (Appendix 3).

Table 4. Soil characterization data from UDSTP* from 10 composite samples from a transect across the study site before FGD gypsum application in January 2012. Rainfall simulation soil was a homogenized composite sample.

Soil	pHw[1]	OM[2] (LOI) %	M3-P	M3-Ca	M3-Mg	M3-Fe	M3-S	M3 Al	Est. CEC[3] Meq/100g	Base Sat. %	P Saturation Ratio[4]	Sand %	Silt %	Clay %
			mg kg^{-1}											
Field Study	**5.2**	**1.7**	**364**	**906**	**97**	286	**21**	797	7.5	**77.8**	**86.0**	51.7	35.1	13.2
Rainfall Simulation	3.6	4.2	54	234	53	300	34	795	7.6	25.9	16.5	53	34	13

* University of Delaware Soils Testing Program, major differences in **bold**.
1 = pH measured in 1:1 soil: water mixture
2 = Organic Matter by Loss-on-Ignition
3 = Cation exchange capacity

Taxonomy

The soil sleeves used for taking the deep cores were 1.04 m in length. When the sleeves were retrieved from the field the soil did not fill the entire length of the sleeve, indicating compaction had occurred in the process of retrieving the cores. On average, soil cores were subjected to 24% compaction, making accurate depth measurements difficult (Fig. 9). It cannot be assumed that the intensity of compaction was consistent throughout the cores, therefore depths indicated in this paper are based on the actual lengths measured while dismantling and analyzing each core. The cores were fairly uniform in texture and color (Fig. 10), with the exception of a clustered few that had substantial amounts of visible charcoal below the Ap horizon, probably an unexplained anthropogenic relic. In regards to the taxonomic class, initially assumed to be primarily Othello based on the USDA-NRCS Soil Survey, the best matched soil series would be Fallsington, due to courser textures than would be expected from an Othello soil. The representative profile description (Table 5) provided by the United States Department of Agriculture/Natural Resource Conservation Service Official Soil Series Descriptions (OSD) matched well to the core descriptions of field samples. Gleying and the strong presence of redoximorphic features were not surprising, given the seasonally high water table and drainage mechanics in the study area. No limiting layers that might affect hydrology were noted, although this would have been difficult to discern on such narrow core samples. See Appendix 2 for brief core descriptions for all cores.

Table 5. Typical profile description from the USDA-NRCS Official Soil Series database for Fallsington.

Fallsington: *Fine-loamy, mixed, active, mesic, Typic Endoaquults*				
Horizon	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	0 to 25	10YR 3/2	sandy loam	
E	25 to 36	2.5Y 6/2	sandy loam	x
Btg1	36 to 50	10 YR 6/2	sandy loam	x
Btg2	50 to 74	2.5Y 5/2	sandy clay loam	x
BCtg	74 to 102	2.5Y 5/2	sandy loam	x
CBg	102 to 178	2.5Y 5/2	loamy sand	x
Cg	179 to 191	2.5Y 5/2	sand	

USDA/NRCS Official Soil Series Description
http://www.nrcs.usda.gov/wps/portal/nrcs/detailfull/soils/home/?cid=nrcs142p2_053587
(last accessed 7 Nov 2014)

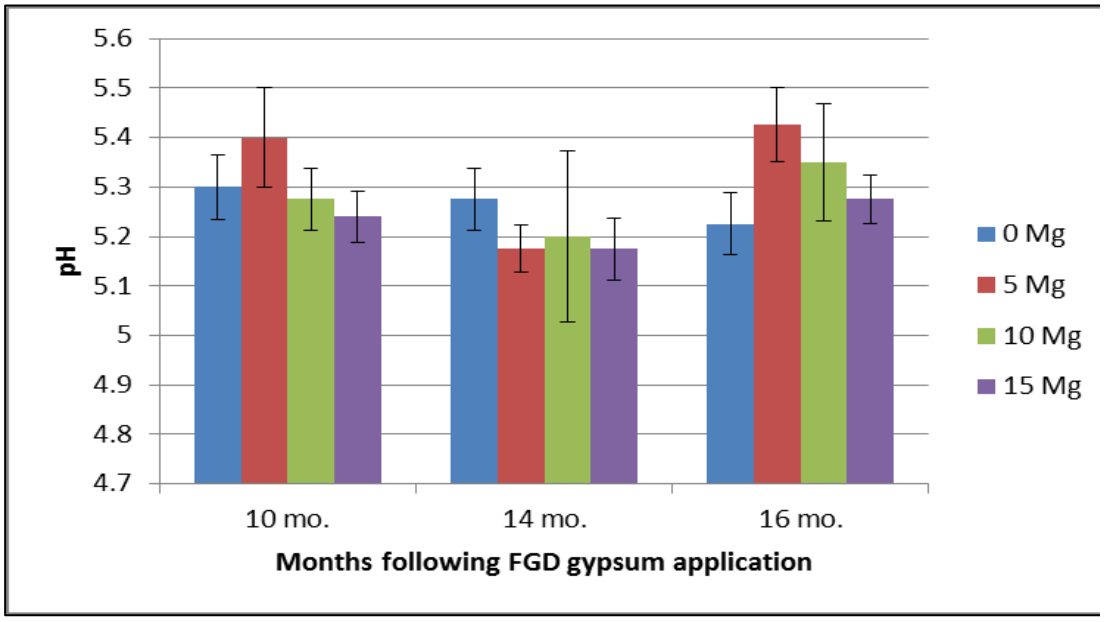


Figure 8. pH values over time and across treatments. FGD gypsum application appears to have not had a significant effect on infiltration.
Bars represent standard error of the mean.

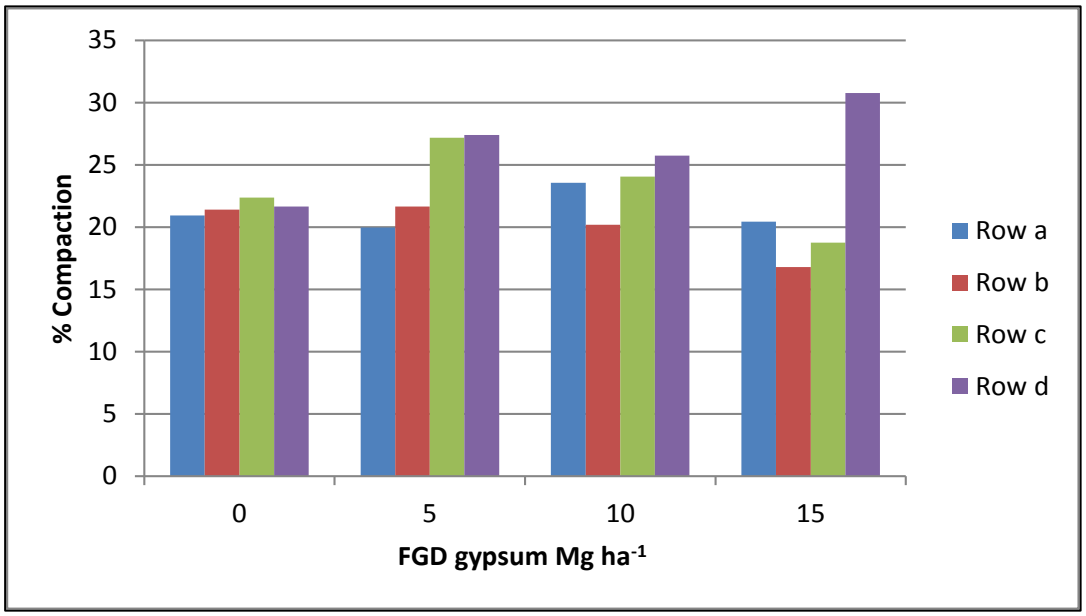


Figure 9. Core sleeves were 1.04 m long, but were subject to an average 25% compaction across cores. Row a, b, c, d indicate location of cores, based on infiltrometer site. (See Fig 3)

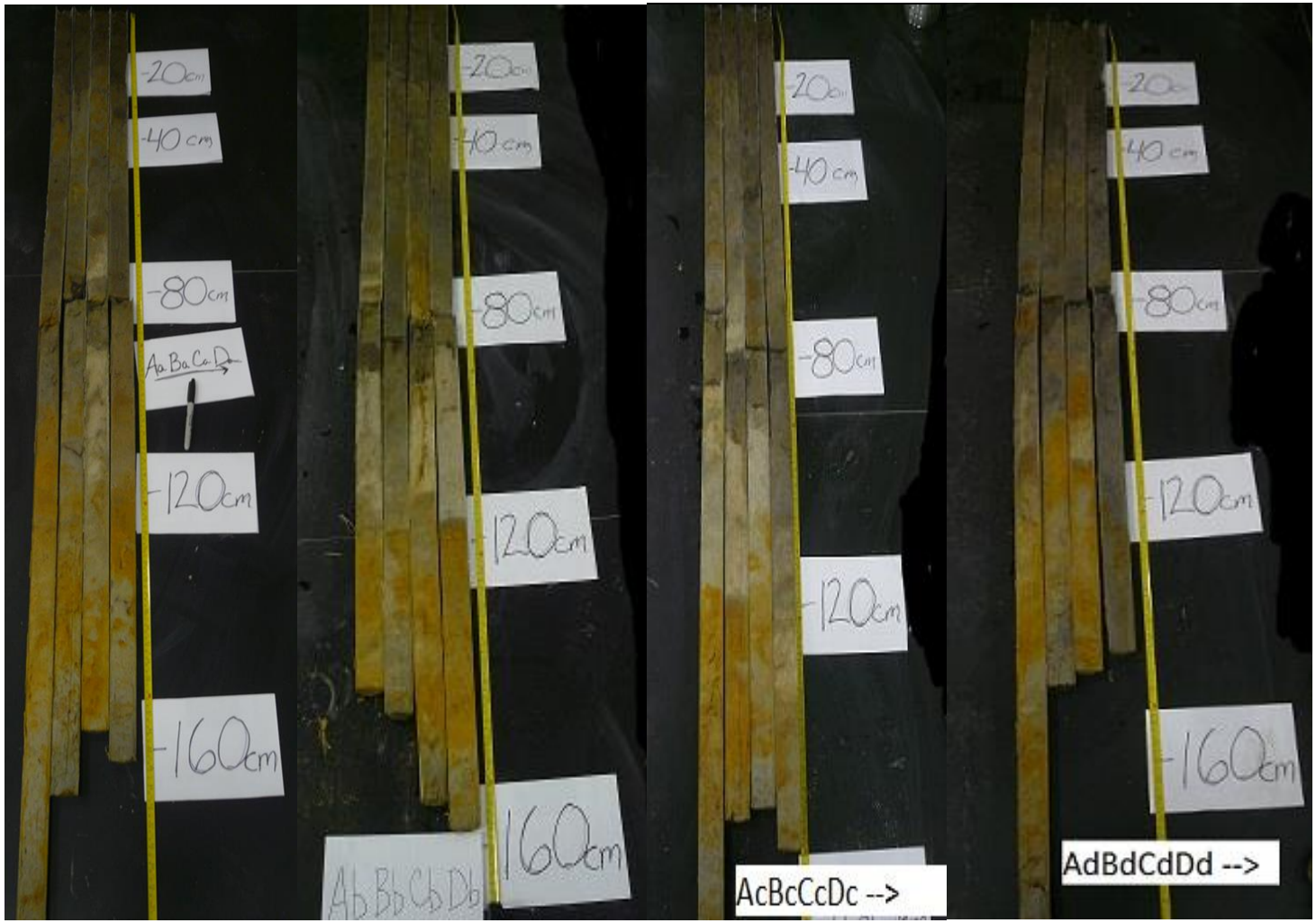


Figure 10. Deep 2 m cores with highly visible Fe concentrations and gleying that would be expected in a location that is flooded and drained regularly. From right to left, are cores taken across treatment rows starting on the southeast edge (a) of the field extending northwest (d). Capital letters A, B, C, D indicate treatment levels 5, 10, 15, 0 Mg ha^{-1}, respectively.

Infiltration

Field Infiltration

Field infiltration data are reported and interpreted here, with acknowledgement that inferring anything beyond the study area is not appropriate due to lack of replication and randomization, and thus were not treated with inferential statistics. Therefore, observational interpretations are made here by comparing mean standard errors. Where mean standard error bars overlap, there is no significant difference. However, if the bars do not overlap, significance cannot be determined due to the reasons listed above. Due to uncertainties in the uniformity of the gypsum application with the manure spreader (University of Maryland Department of Environmental Science and Technology, 2012), I intended to explore the relationship between infiltration rates and the amount of exchangeable Ca at specific infiltrometer sites. Data for exchangeable Ca followed the general trend of the treatment levels as applied (Fig. 11), however there was no correlation between exchangeable Ca and FIR (Fig. 12).

The data from March 2012, two months after FGD gypsum application, did not demonstrate a significant difference between treatments for FIR. Among the four treatments, the control had the highest mean, although it was not significantly different from either the 5 or 15 Mg ha^{-1} treatments (Fig. 13). The 10 Mg ha^{-1} treatment demonstrated the lowest FIR. Although not significantly lower than the 15 Mg ha^{-1} treatment, it was apparently lower than the control. Since there is no discernable trend for the treatment level effects, the difference between the control and the 10 Mg ha^{-1} treatment level may simply indicate differences in hydrology across the field. As this was not controlled in the experimental design, it is difficult to draw any specific conclusions.

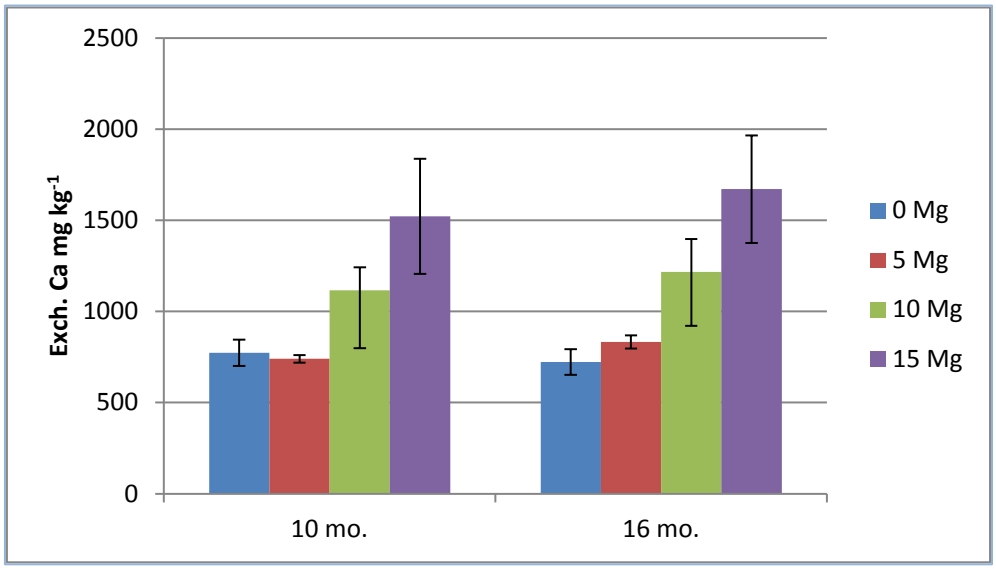


Figure 11. Exchangeable Ca across FGD treatment levels.
Bars represent standard error of the mean.

There was an apparent difference between treatments in Fall 2012, about ten months after application. The higher infiltration rate across all treatments was almost certainly due to seasonal fluctuation in antecedent moisture (Fig. 14). Although soil moisture content readings were not taken at the time, the post-harvest soil in the fall was visibly much drier than it was in the spring, which typically coincides with the seasonal high water table. Based on the change in FIR across all treatments from one season to the next, it seems soil moisture had some effect on FIR (Fig. 14). The control treatment is still higher than the 5 and 10 Mg ha^{-1} conditions, but lower than the 15 Mg ha^{-1} treatment. Additionally, the difference in raw FIR within treatments across seasons would indicate that there may have been an increase in FIR in the 10 and 15 Mg ha^{-1} treatments that cannot be completely explained by seasonal fluctuations. By May 2013, 16 months post-application, there was no difference between treatments.

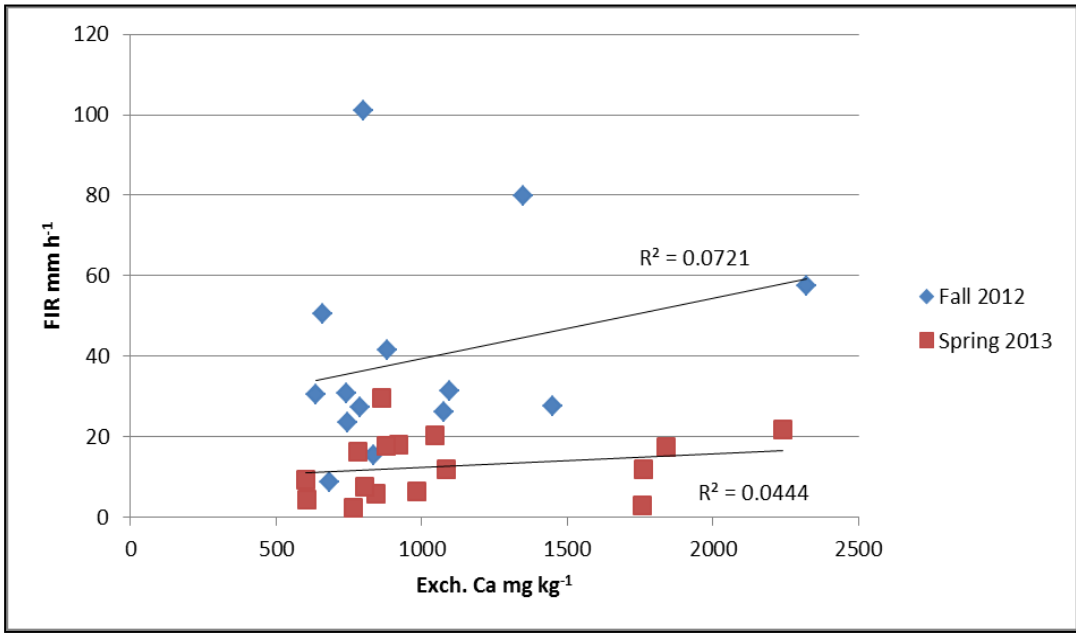


Figure 12. Exchangeable Ca vs data for final infiltration rate separated by time after application of FGD gypsum.

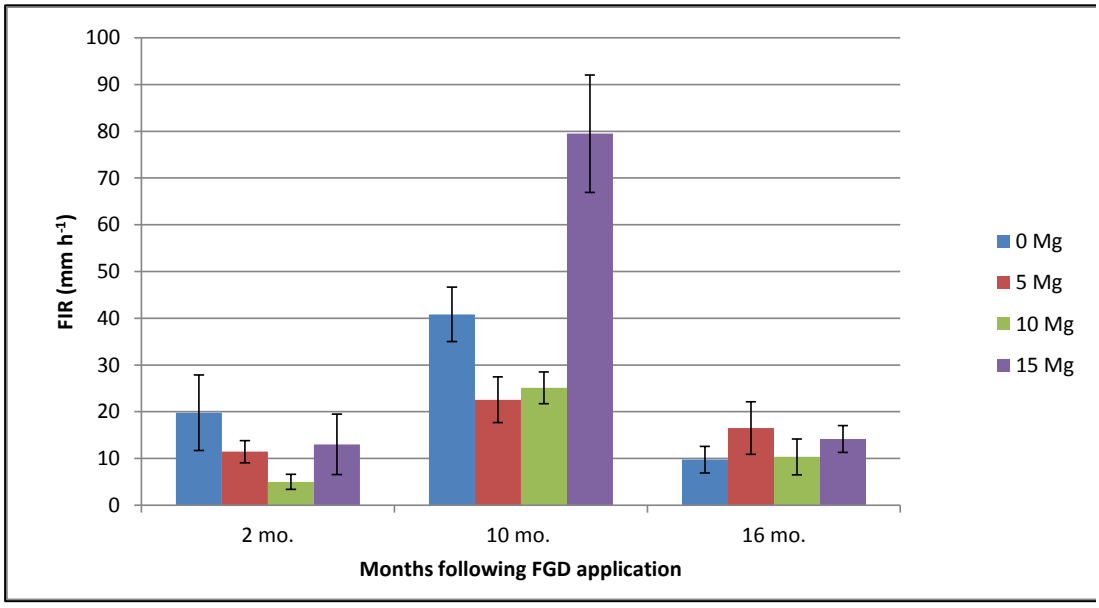


Figure 13. Infiltration data grouped by season, indicated as months following FGD gypsum application in Mg ha^{-1}. March 2012, November 2012, and May 2013 are represented by 2, 10, 16 mo., respectively. The soil was much drier for the November field sampling than either the previous March or May of the following year.
Bars are standard error of the mean.

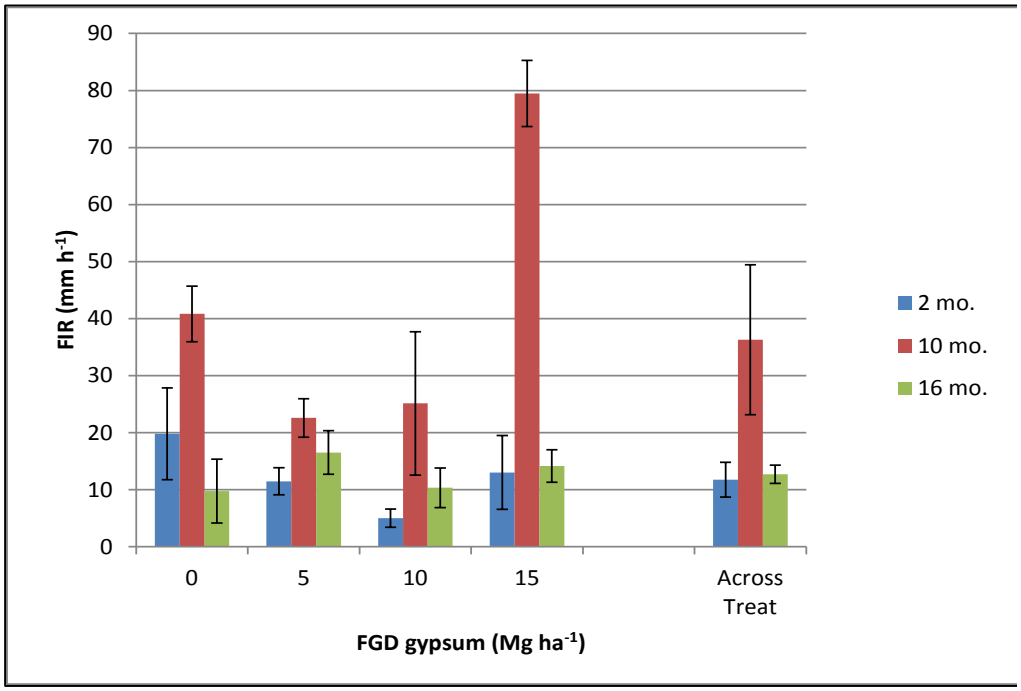


Figure 14. Infiltration rate data by treatment level showing seasonal variation in infiltration. If FIR for all treatments is averaged across treatments, the seasonal effect is clear.
Bars are standard error of the mean.

The Philip equation was applied to the infiltration data to obtain the parameters needed to model the infiltration curves. Even if FIR was not significantly different between treatments, there is potential for the infiltration curves to be different. FGD gypsum has been shown to slow the decline of infiltration over time (Warrington et al., 1989; Yu et al., 2003). The two highest treatments demonstrated more gradual slopes in the spring of 2012 (Fig. 15a), although in Fall 2012 the 15 Mg ha^{-1} treatment had the steepest curve, in contrast to what one would expect if treatments were having the expected impact (Fig. 15b). In spring 2013 the slopes of the two highest treatments (Fig. 15c) also have the more gradual slopes. In summary, there is no evidence that FGD gypsum has affected the decline in IR over time.

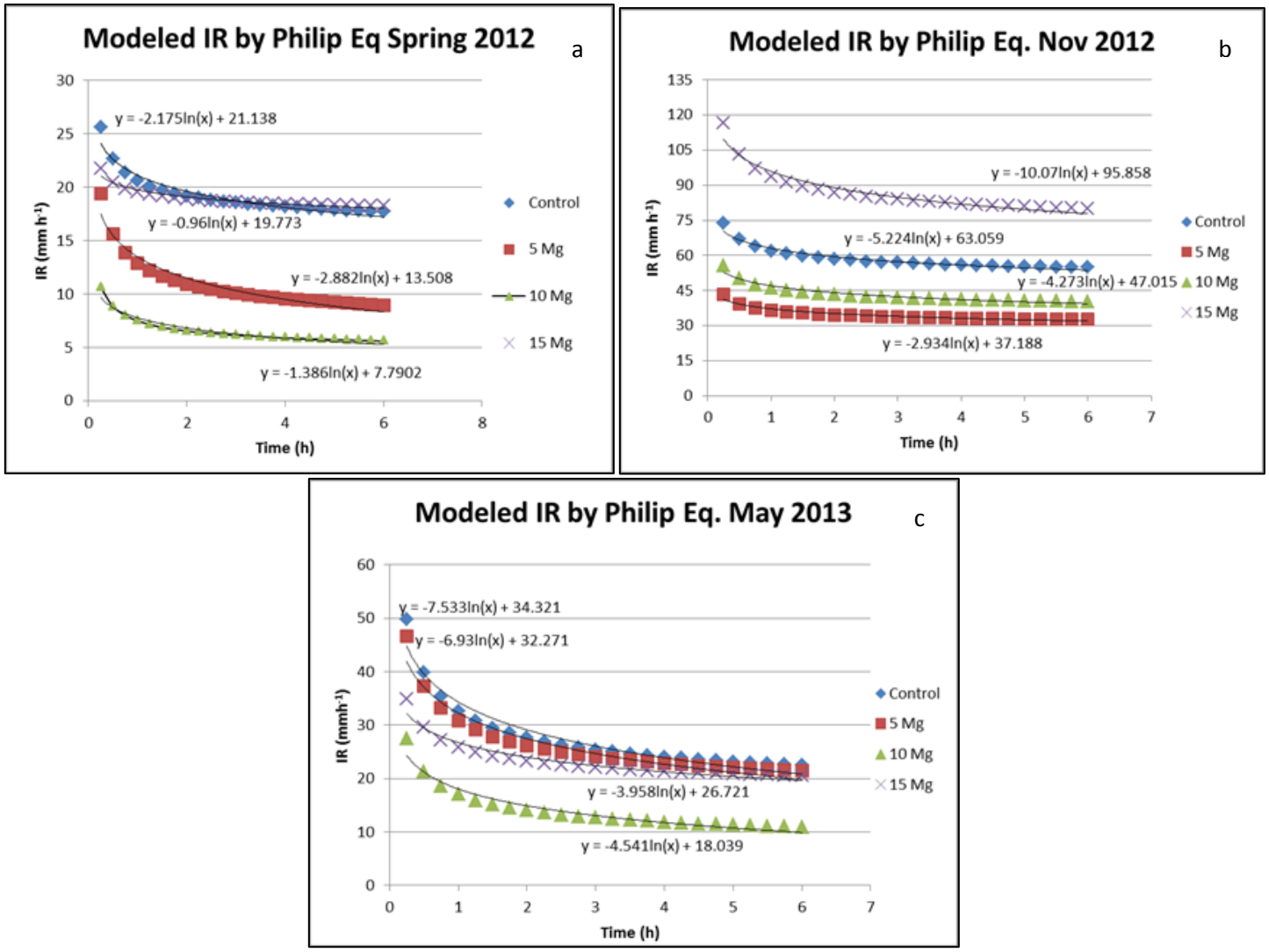


Figure 15. Infiltration curves modeled using the Philip equation for (a) 2 months (b) 10 months and (c) 16 months after FGD gypsum application.

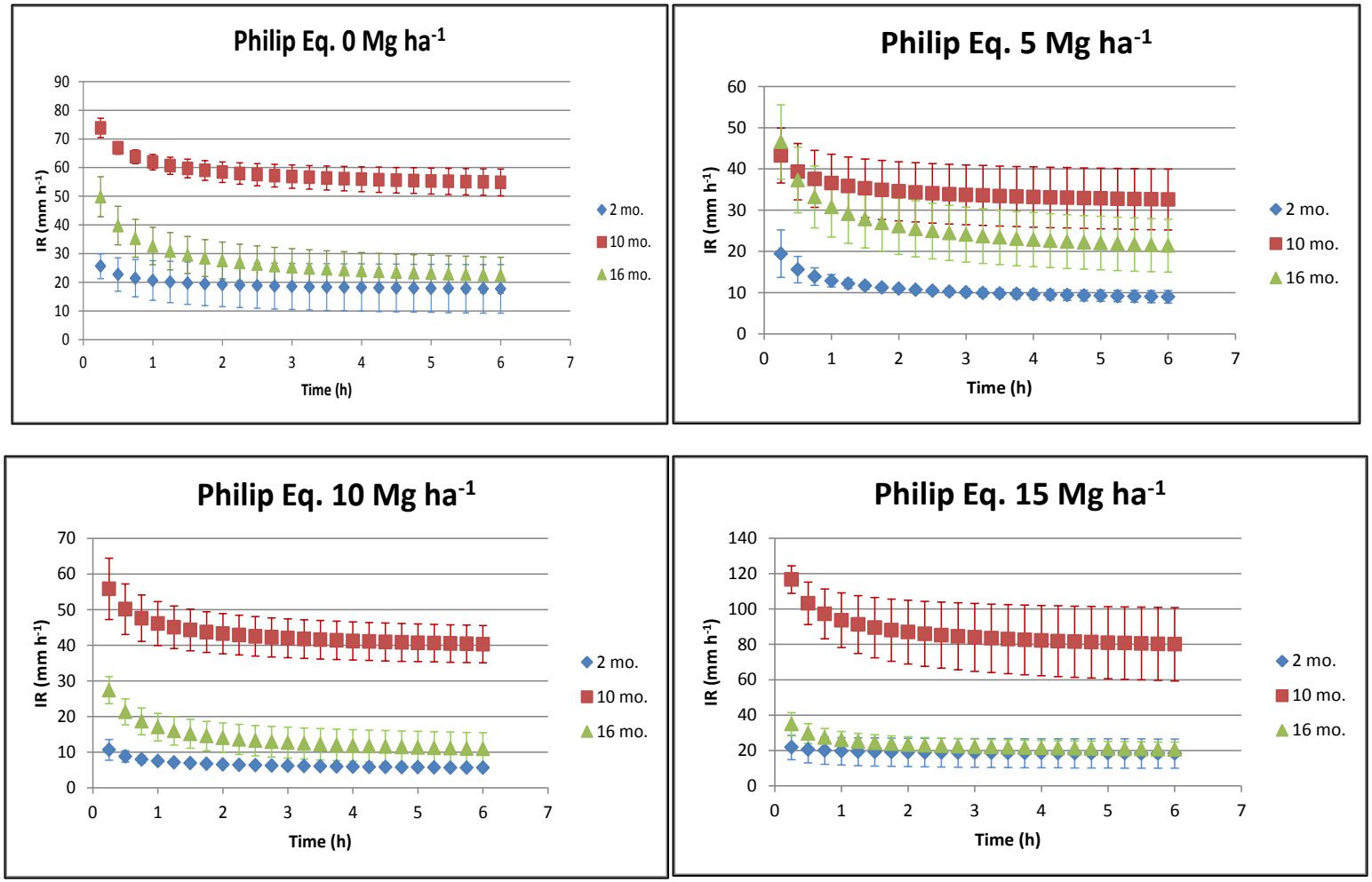


Figure 16. Infiltration data fitted to the Philip Equation. Each set of curves indicates one FGD treatment level across seasons: 2, 10, 16 mo. after FGD gypsum treatment. Infiltration rate is much higher at 10 mo. Post- FGD application for all but the 5 Mg ha^{-1} treatment. For R^2 values for specific curves see Appendix 4.
Bars are standard error of the mean.

FIR, modeled by the Philip equation, resulted in similar trends to those of the raw field data. Comparison within treatments and across seasons shows higher infiltration during the fall of 2012 season for all treatments (Fig. 16). Extrapolating anything specific from these trends is not possible due to the lack of replication or randomization. Extraneous factors, such as seasonal fluctuations in water table, bulk density, root penetration, and soil variability were not taken into account. The best approach is to compare the relative changes using the control treatment as a baseline. With the modeled FIR, I used the between-season differences of the control treatment in order to determine whether an apparent difference between treatments could be argued on a season-by-season basis. By comparing the seasonal changes in FIR within the control treatment to the seasonal differences within the remaining treatments, one could conclude that the 10 and 15 Mg ha^{-1} treatments did show a change in FIR by season greater than the control (Fig. 17), by approximately 5 and 10 mm h^{-1}, respectively. These application rates are far greater than other published research indicating effectiveness of gypsum at rates as low as 2 to 5 Mg ha^{-1} (Ben-Hur et al., 1992; Keren and Shainberg, 1981; Miller, 1987; Yu et al., 2003). By May 2013, about 16 months after initial application there was no significant difference between treatments, possibly indicating that any effects of the FGD gypsum on infiltration rate have diminished. The substantial drop in FIR from fall 2012 to spring 2013 at the 15 Mg ha^{-1} level boosts the possibility that the FGD gypsum may have been responsible for increased infiltration.

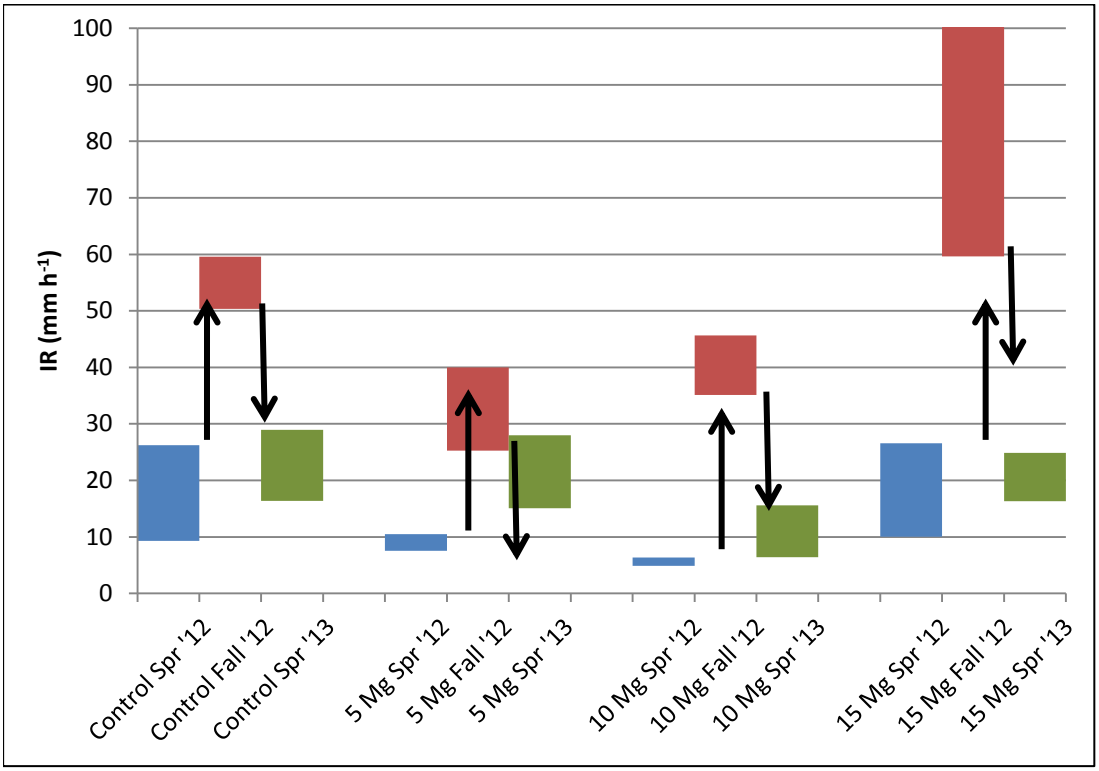


Figure 17. The colored blocks represent the area between the ± mean standard error for final infiltration rate (FIR). Arrows are used as a visual representation of the seasonal change in FIR for the control treatment and are juxtaposed against the seasonal changes within the other treatments. The lack of overlap between the arrows and blocks indicate that 10 and 15 Mg ha^{-1} treatments demonstrate slightly more seasonal variation than the control, possibly indicating FGD gypsum has an effect on the FIR.

The key to gypsum effectiveness in improving the structure of a sodic soil is attributable to the added Ca. Calcium replaces Na cations on soil colloidal surfaces to create a tighter bond between clay sheets, providing a more rigid structure and reducing slaking. These changes allow direct paths for water infiltration (Brady and Weil, 2008b). However, the more humid regions of the Mid-Atlantic differ in parent materials and geologic history and are not prone to Ca deficiencies. Additionally, decades of poultry litter application have resulted in even higher rates of Ca then would naturally be present. Typical broiler chicken poultry litter has been reported to contain 44 lbs of Ca per ton and many thousands of tons of litter may be produced every year at a given facility (Chastain

et al., 2001). Analysis of the field soil in this study showed a three-fold increase on M3-Ca due to long-term manure application (Table 4), as compared to adjacent soil used in rainfall simulation.

K_{sat} in the lab between treatments was found to be more or less the same, with the exception of the 10 Mg ha^{-1} treatment (Fig. 18), which was apparenty lower than the others. Between 1.5 and 5.1 mm h^{-1} is considered slow K_{sat} by USDA standards and generally associated with clayey soils (U.S. Department of Agriculture-Natural Resource and Conservation Service, 2014a). The mean K_{sat} was 3.63 mm h^{-1}, indicating that a high bulk density must have played a role in determining the K_{sat} here. The calculated K_{sat} values for the soil columns are far lower than the transmissivity (A) parameter calculated using the Philip Equation parameters found in the field experiment. Since not all soil pores will conduct water in a real system, it is sometimes useful to calculate a mean pore water velocity ($\bar{v}$), by dividing q (Darcy's velocity) by Θ (mean volumetric water content) (Hill, 2012), which will inevitably be higher than K_{sat} (Table 6).

There was not a significant difference in bulk density by treatment (Fig. 19). Mean bulk density was 1.56 g cm^{-3}, which is just within the high end of the range for optimum plant growth (U.S. Department of Agriculture-Natural Resource and Conservation Service, 2014b). As has been mentioned, this data likely does not accurately reflect the bulk density at the time of infiltration readings for two reasons: surface bulk density is subject to seasonal variation (Hu et al., 2012) and it can be significantly increased by land-leveling (Öztekin, 2013). Little if anything can be drawn from this data because the cores were retrieved after the property owner land-leveled the

field, in part due to concerns regarding variable drainage and ponding, thus illuminating the need for a randomized experimental design.

Table 6. Water Movement in Field Soil

FGD gypsum treatment Mg ha^{-1}	Ksat[1], Soil Columns	$\bar{v}^2$	Raw Field FIR			Parameter A (Transmissivity) Field Data		
	mm h^{-1}							
	June 2013 Post land-level		Mar 2012	Nov 2012	May 2013	Mar 2012	Nov 2012	May 2013
Zero	3.96	29.30	19.8	40.8	7.8	15.62	50.00	10.50
Five	4.19	30.88	11.5	22.3	13.2	6.30	29.85	14.93
Ten	2.05	15.55	5.0	20.1	8.3	4.32	36.33	6.68
Fifteen	4.35	33.71	19.0	52.8	15.0	17.81	70.67	16.82
Mean	3.63	27.36	13.5	39.4	12.7	11.54	45.91	12.23

1= Saturated Conductivity
2= Mean Pore Velocity

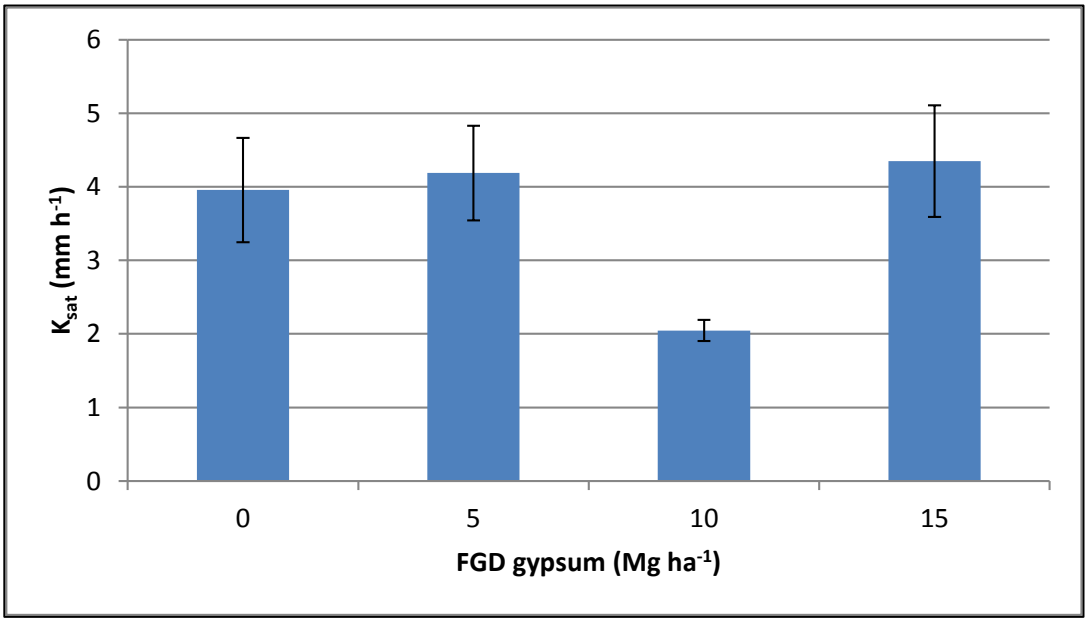


Figure 18. Saturated hydraulic conductivity by treatment. Cores were retrieved after land-leveling of the field site, likely affecting the results.
Bars are standard error of the mean.

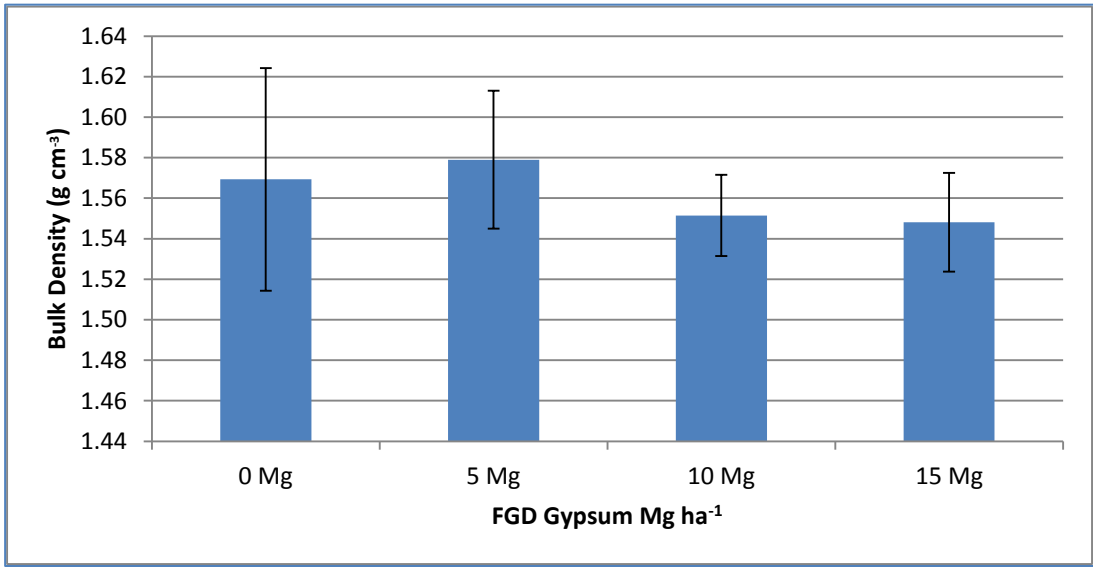


Figure 19. Bulk Density taken only weeks after land-leveling of the field site, therefore the soil is likely more compacted than usual.
Bars are standard error of the mean.

Rainfall Simulation

Results for the rainfall simluation were unexpected. There was no statistical difference between the control and 30 Mg ha^{-1} treatment (Fig. 20), although all other treaments appeared to have significantly lower FIRs than the 30 Mg ha^{-1} treatment. Additionally, the 10 and 15 Mg ha^{-1} treatments each had a significantly lower FIR than the control. Fitting of the data to the Philip equation validates the same result (Fig. 21), essentially a trend opposite of what would be expected. There is research on the potential dispersive effects of sulfate as an anion. The quantity of sulfate needed for this effect to occur is far more than what was in this soil (Nguyen at al., 2013). One explanation is FGD gypsum simply did not effect infiltration rates in the soil, another is that the method used for the rainfall simulation may have not been appropriate for what I sought to measure and the methods used were easily subject to error. I attempted to pack the boxes to a specific bulk density, but this was difficult due to slight variations in the size of each box. Additionally, the coefficient of variation for the rainfall simulator was not ideal, ranging from 0.91 – 0.97 depending on the position of the trays. An additional consideration is the chemical differences between the soil used in the lab simulation, compared to the soil used in the field study, based on the history of use. The lab soil was taken from an adjacent field, which was of similar texture and similar in some of the elemental composition, but was far lower in regards to pH and Ca, and and higher in OM content (Table 4). Analysis of variance did not indicate that there was a significant difference between treaments ($p > 0.1$).

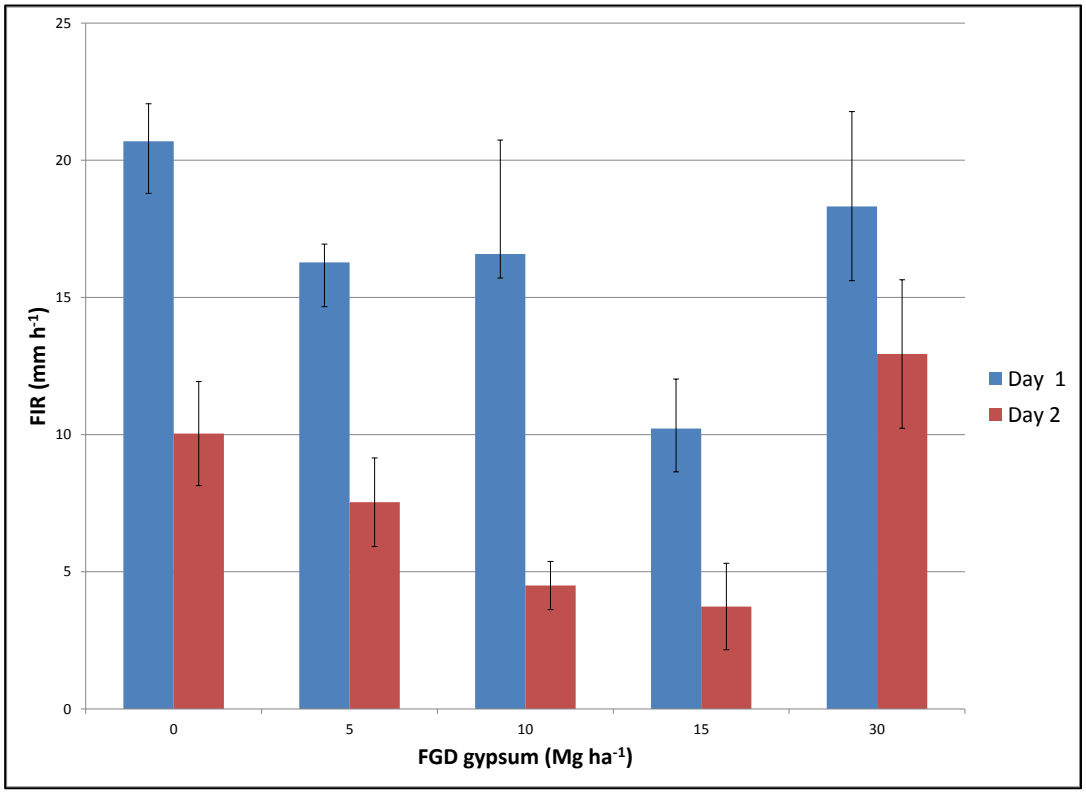


Figure 20. Raw final infiltration rate for rainfall simulation.
Bars are standard error of the mean.

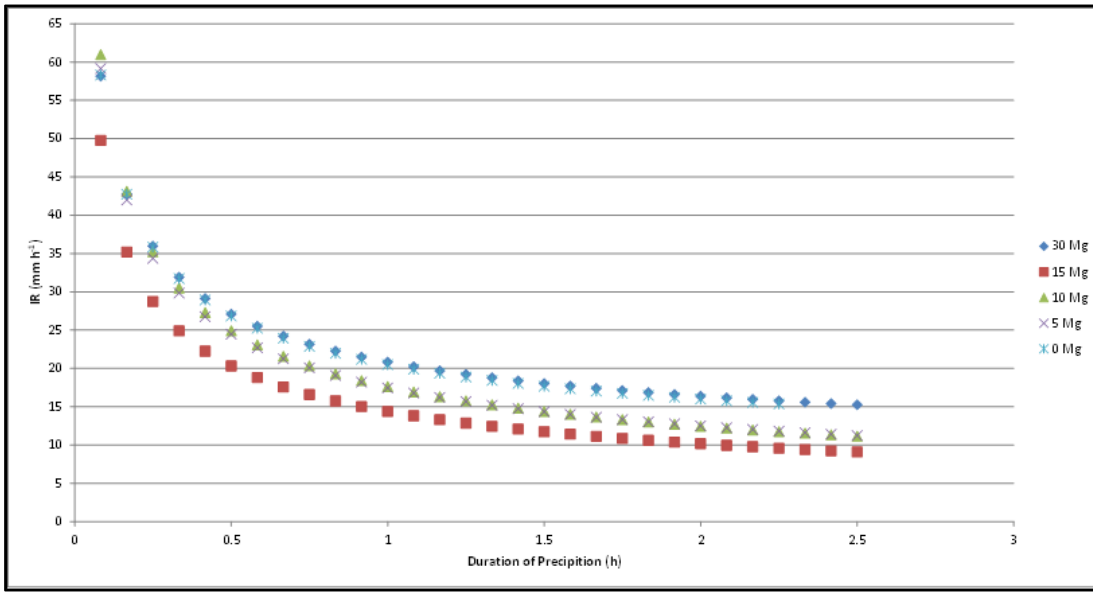


Figure 21. Infiltration curves from rainfall simulation modeled by with the Philip Equation. Analysis of variance showed no significant difference in FIR for the treatment levels ($p>0.01$).

Phosphorus

Water Extractable Phosphorus

WEP data were analyzed at three different labs, each reporting slight differences in WEP. Each lab reported a general decline in WEP with higher FGD gypsum application. The transect collected in Jan 2013 (Set C, USDA-ARS) demonstrated a 7-48% decrease in WEP by treatment (Fig. 22a), while the differences in WEP for the UDSTP (Fig. 22b) and UMCP (Fig. 22c) data were weaker, likely attributable to the small sample size per season (n=16). By May 2013, WEP content is similar to the control for both the UDSTP and UMCP data, indicating any effects on WEP had diminished, similar to findings from Johnson et al. (2011), who reported effects on WEP diminished substantially by the second year of a field study on soils of the Lower Eastern Shore of Maryland. There was a discernable, but weak linear relationship between exchangeable Ca and WEP ($r^2 = 0.35$, Fig. 23). Regardless of the variation among lab results, the results indicated at least a temporary decrease in WEP after FGD gypsum was applied.

WEP content at both USDA-ARS and UDSTP was analyzed using ICP, while analysis at UMCP was done by colormetric analysis. There is some debate over which of these analytical methods is best for detecting WEP (Pierzynski et al., SERA 17; Self-Davis, 2009; Wolf et al., 2005). The USDA-ARS had a larger sample size (n=40) and was not retrieved at the same time of the year. It could be perceived that UDSTP retrieved slightly more WEP than UMCP for the Nov 2012 and May 2013 samples with ICP analysis, but a larger sample size would make this clearer.

The acidic soil may contribute to the short-lived effects of FGD gypsum on WEP. In acid soils, aluminum and iron phosphate precipitation will dominate (Penn et al., 2007). At pH levels of pH 6.3 and above, Ca-P precipitation dominates, far above the average soil pH of 5.2 reported here (Lindsay, 1979; Greenwald, 1942). Therefore, it is plausible that initial quick precipitation reactions between soil P and added Ca dissipated over time, as equilibrium was re-established in the soil environment, and assuming that the availability of Al and Fe sorption sites has not changed (Table 4).

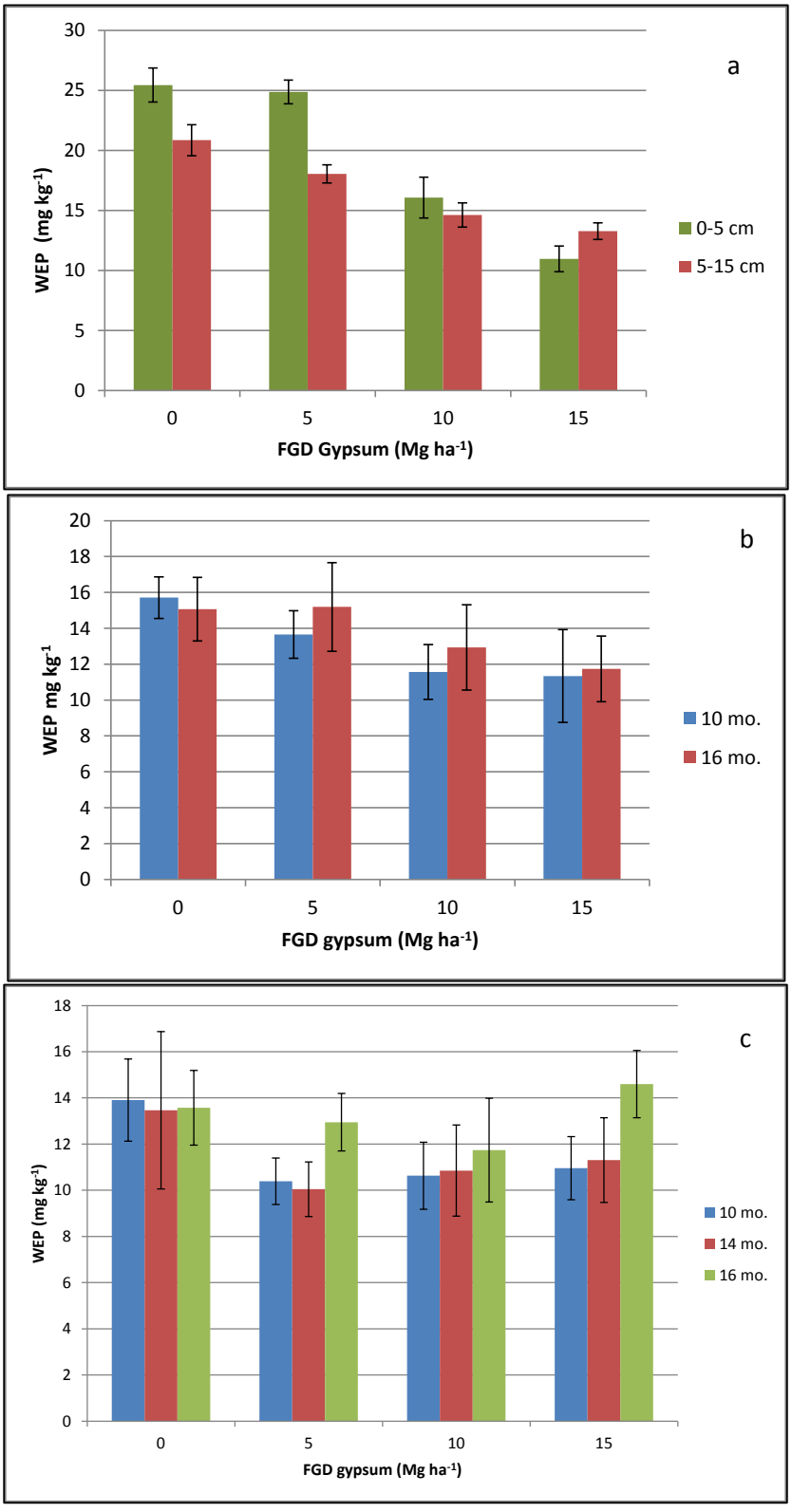


Figure 22. Water Extractable Phosphorus results from three different labs. (a) One-year post-FGD gypsum application, n=40, USDA-ARS; (b) 10 and 16 mo. post-application, n=16, UDSTP; (c) 10, 14, 16 mo. post-application, n=16, UMCP. Bars are standard error of the mean.

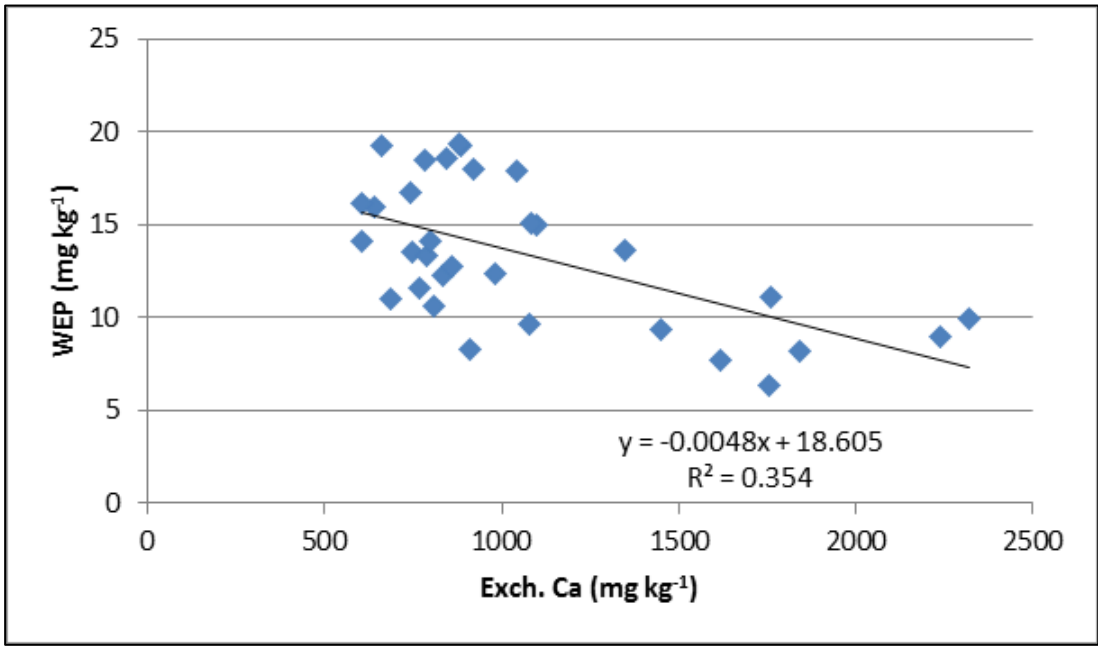


Figure 23. Exchangeable Ca data from Nov 2012 and May 2013 vs. water-extractable phosphorus (WEP).

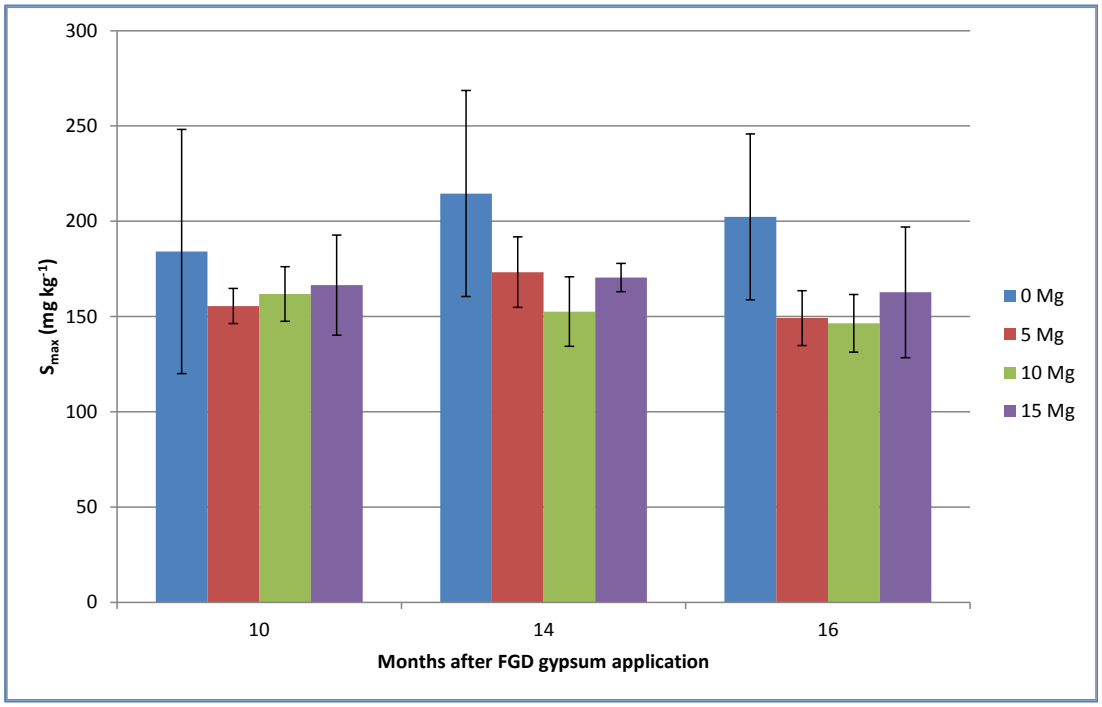


Figure 24. P sorption maximum as indicated by the Langmuir sorption model. Bars are standard error of the mean.

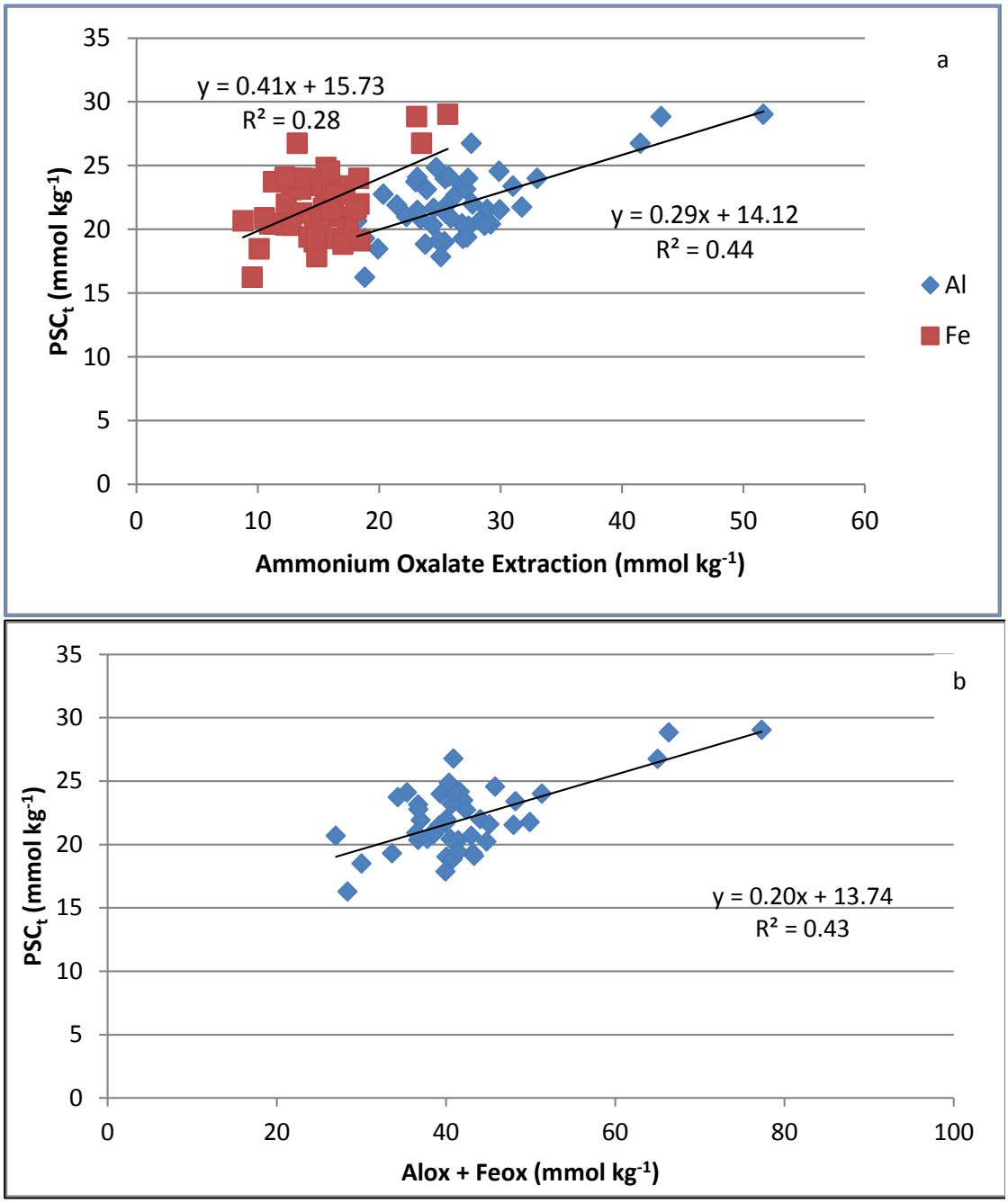


Figure 25. PSCt = Pox + Smax; (a)PSCt compared separately to Feox and Alox; (b) there is a weak positive relationship between total P sorption capacity and Alox and Feox indicating that there are other substantial factors responsible for P sorption.

P Sorption

S_{max} values for P sorption calculated by the Langmuir model showed no difference between treatments in the Fall of 2012, however S_{max} did appear higher for the control than the FGD treatments for both 14 and 16 months after FGD gypsum application (Fig. 24). Why would that be the case?

Pautler and Sims (2000) suggested that soils low in Al and Fe would have a higher percentage of easily desorbed P. They defined phosphorus sorption capacity (PSC_t) as the sum of P_{ox} and S_{max} and found a significant correlation between PSCt and the sum of Al_{ox} and Fe_{ox} ($r = 0.61$), lending credence to low OM soils being controlled by Al and Fe. I found a weaker linear

relationship ($r^2 = 0.43$, Fig. 25b). Theoretically, an increase in P_{ox} would result in a decrease in S_{max}, assuming that PSC_t does not change. Therefore I separated the P_{ox} by season (Fig. 26a), but did not interpret any kind of pattern to explain S_{max}. Research suggests that Al has more of a hand in sorption capacity than Fe (Maguire and Sims, 2002). The linear relationship between PSC_t and Al_{ox} is in fact stronger that PSC_t and Fe_{ox} (Fig. 25a). There is a slight decrease in Al_{ox} (Fig. 26b), as FGD treatment level increases. Interestingly, the proportion of Alox decreased with increased FGD gypsum (Fig. 26c).

All alpha values where within a range of 0.3 – 0.8, slightly wider than reported by Sims et al. (2002) of 0.4-0.6. The mean alpha value was 0.54 (Fig. 27). DPS_{ox} values were calculated both with $\alpha = 0.5$, the default used in many studies, and individually calculated alpha values. The average difference in DPS_{ox} values calculated by the two different alphas was 10%. Also, using 0.5 as the alpha value underestimated DPS_{ox} in

39% of the samples. For the remainder of this paper, I will use the individually calculated alpha values in calculations of DPS_{ox}.

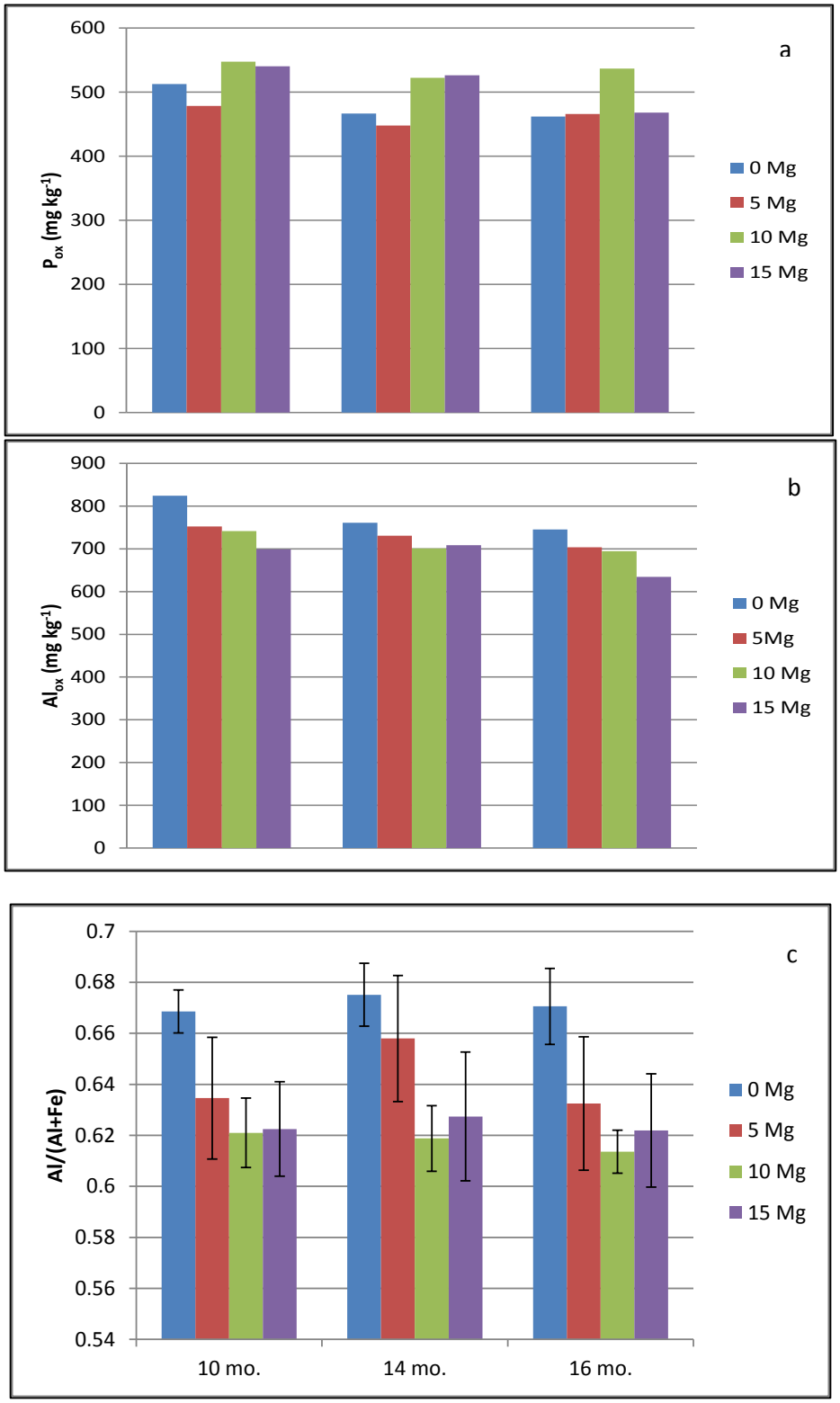


Figure 26. Oxalate extraction of (a) Pox, (b) Alox, and (c) Proportion of Alox + Feox that is Alox, by FGD treatment and season.

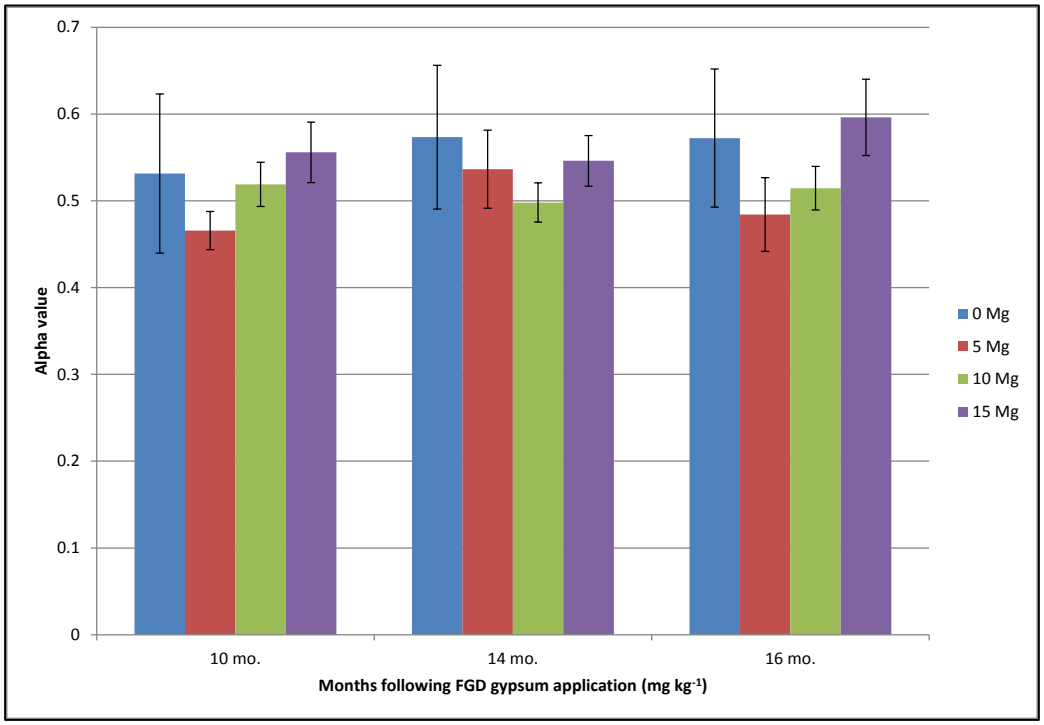


Figure 27. Alpha values for DPS_{ox} by season and treatment: α (Al_{ox} + Fe_{ox}) = P_{ox} + S_{max}
Bars are standard error of the mean.

P Indicator Relationships

It has been suggested that a shift occurs in P associations from Al and Fe to Ca in soils that have received manures additions for many years (Sharpley et al., 2004). In some cases, soils receiving long-term manure treatments have shown DPS values of greater than 100% (Dou et al., 2007), possibly suggesting that Ca-P compounds may be responsible for some of the saturation capacity. Sharpley et al. (2004) surmised that soils subject to long-term manure additions (and high P) may be subject to more Ca-P forms that are not necessarily extractable by water, thus acid extractions such a M3 may over-estimate P loss potential as it pulls P from Ca-P bonds in the soil. They found that WEP and M3 were closely related (r^2 = 0.94) on a curvilinear aspect, indicating that the

proportion of WEP decreased with increasing M3-P. Sims et al. (2002) showed a linear relationship between M3-P and WEP (r^2 = 0.68), although less when separated out by topsoil (r^2 = 0.58). It appears there was not a strong linear relationship between WEP and M3-P (Fig. 28) when the data is taken as a whole, but Figure 29 indicates that FGD gypsum application weakens the relationship between WEP and M3-P.

On the other hand, Sharpley et al. (2004) did find the proportion of M3-P that is water extractable to be negatively correlated to exchangeable Ca (r^2 = 0.89), indicating a strong role for exchangeable Ca in water solubility of P. Field samples did indicate a slight increase in M3-P as FGD gypsum treatments increased (Fig. 30). Although there was not a convincing linear relationship between exchangeable Ca and M3-P (Fig. 31), I did find a negative linear relationship between proportion of M3-P as WEP and exchangeable Ca (Fig. 32), substantiating their previous findings.

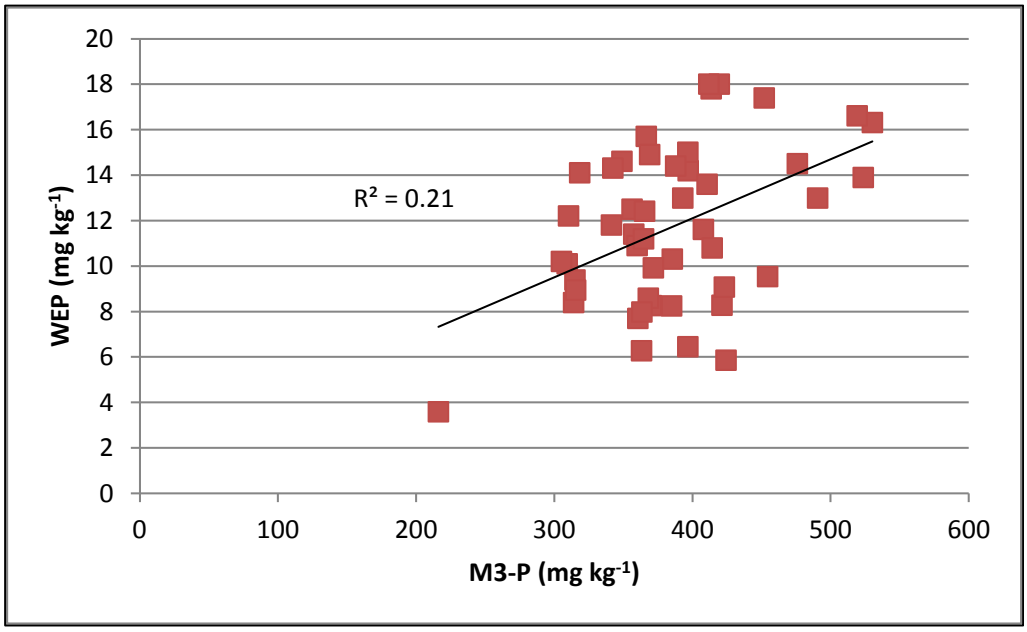


Figure 28. Mehlich 3-P vs. Water-extractable P.

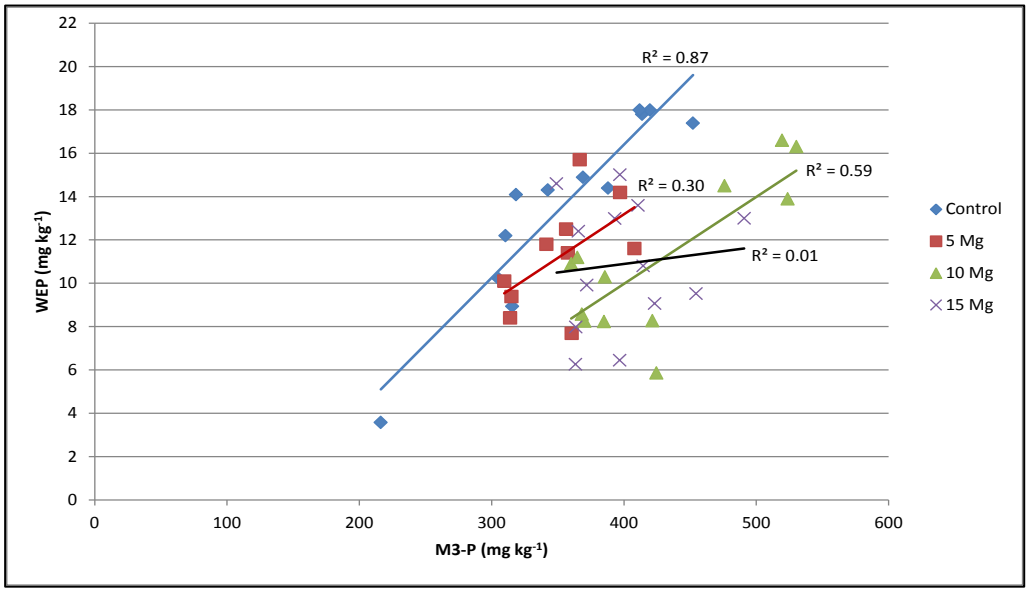


Figure 29. Mehlich 3-P vs. Water-extractable P by treatment. Each treatment includes data from Nov 2012, March 2013, and May 2013 (10, 14, and 16 months after FGD gypsum application, respectively).

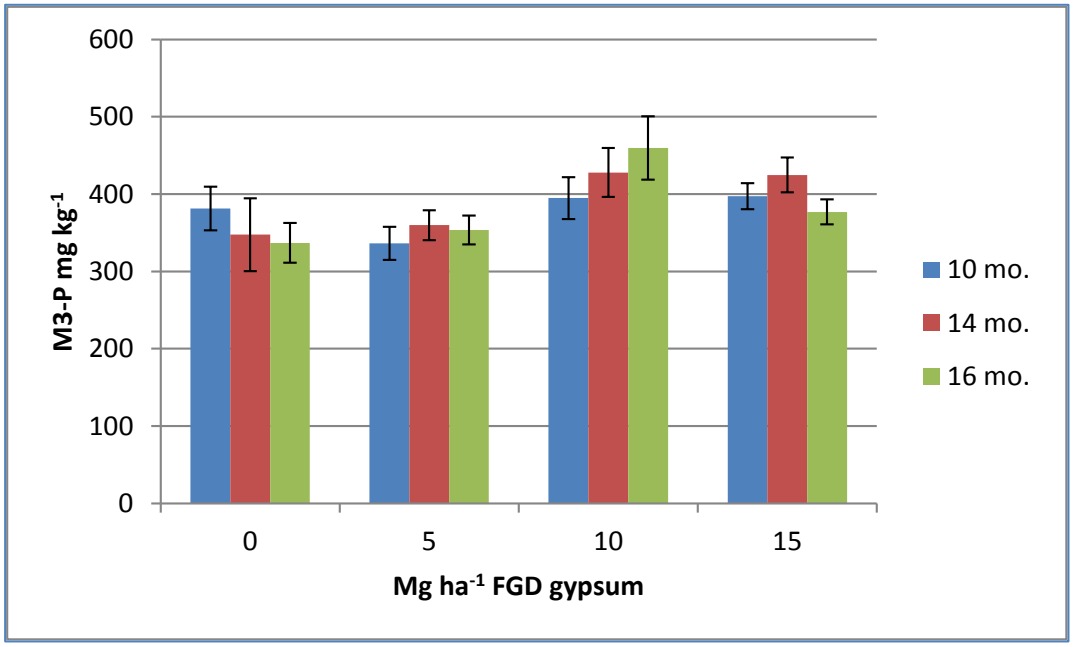


Figure 30. Mehlich 3-P by FGD treatment and season.
Bars are standard error of the mean.

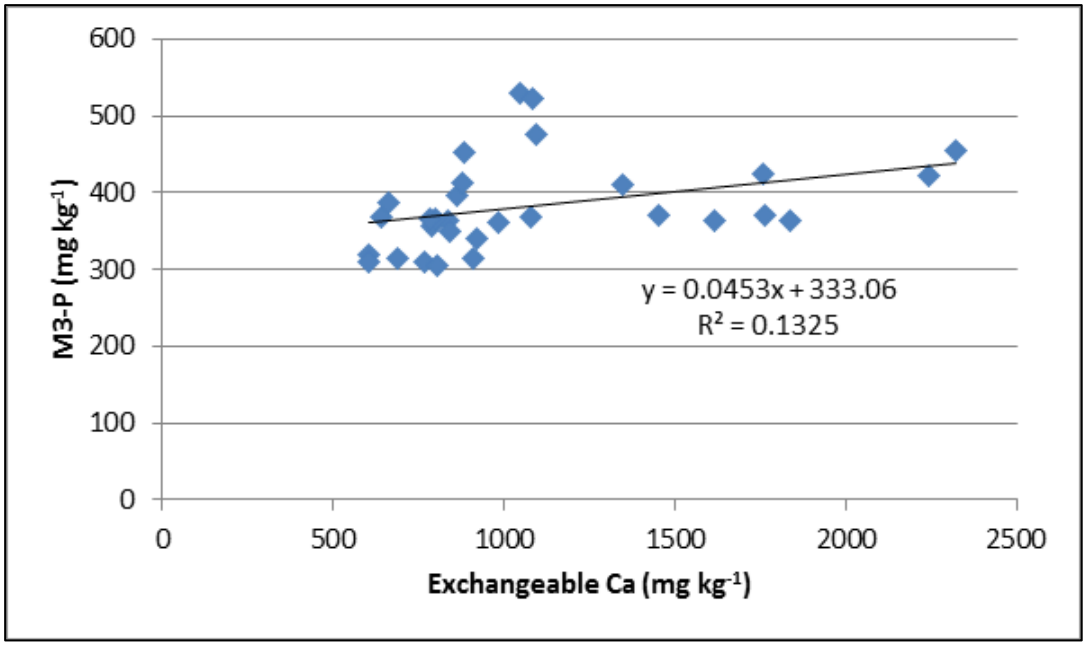


Figure 31. Exchangeable Ca vs. Mehlich 3-P

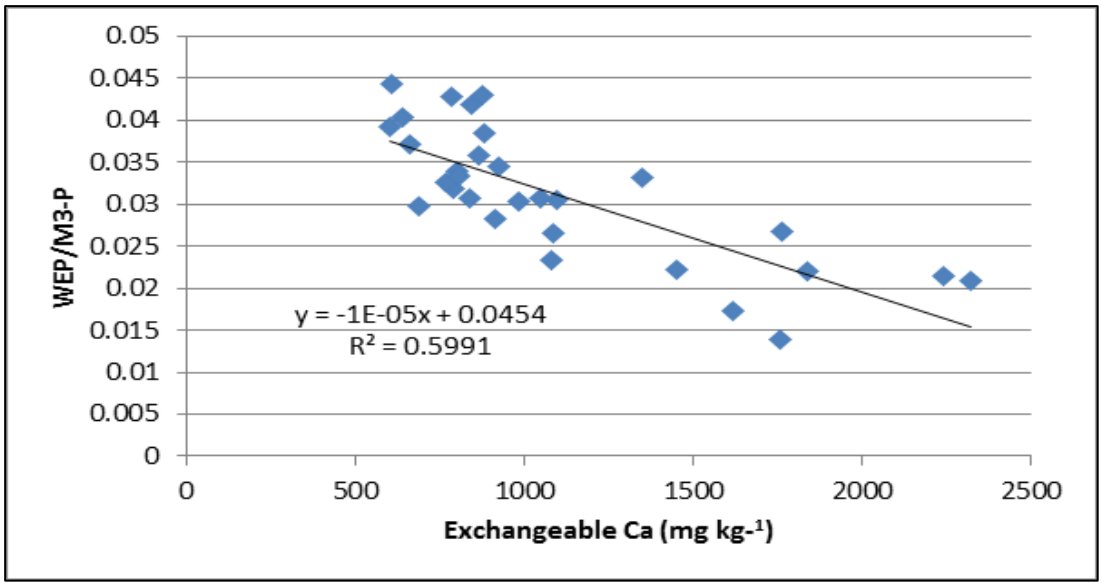


Figure 32. Exchangeable Ca vs. the proportion of Mehlich 3-P (M3-P) that is water-extractable P (WEP)

Linear relationships were found between M3 and oxalate extractions of Al and P (r^2 = 0.83 and r^2 = 0.56, respectively), but not for Fe (Fig. 33). It is striking that M3-Fe varies so little, also evident in the very small mean error for M3-Fe in Figure 31. Sims et al. (2002) had better Al, P, and Fe correlations (r = 0.85, 0.71, and 0.44). Maguire and Sims (2002) found a relationship between M3-Al and Fe and their ammonium oxalate counterparts (r = 0.93 and 0.87, respectively), but showed M3 extracting less Al relative to oxalate at higher P concentrations. I did not have a wide enough variety in P concentrations to test this theory, but this study showed more Al extracted by M3 than ammonium oxalate (Fig. 34). They argued that it is important to include Fe in calculated DPS with oxalate extraction, due to the relatively higher amounts of Fe extracted by oxalate compare to M3. Data here also showed greater Fe extracted by oxalate then M3 (Fig. 34). Sims et al. (2002) showed a linear relationship between M3-P and and DPS_{ox} (r^2 = 0.72). This relationship was far less convincing than for the data here, (r^2= 0.43, Fig. 35).

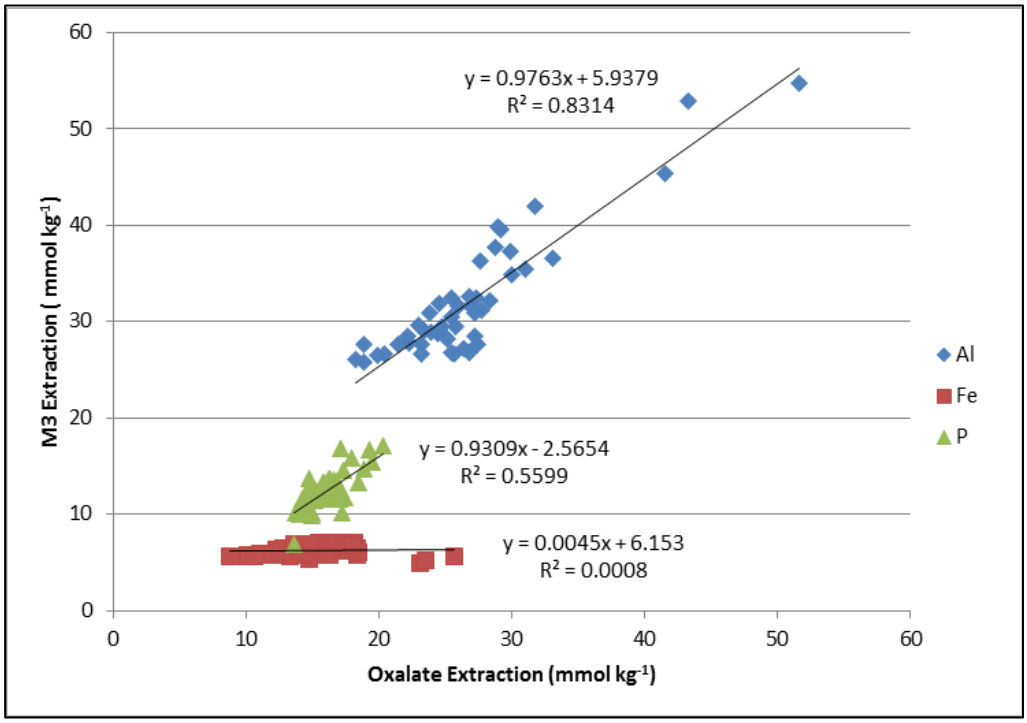


Figure 33. Ammonium oxalate extraction vs. Mehlich 3 (M3) extraction of Al, Fe, and P.

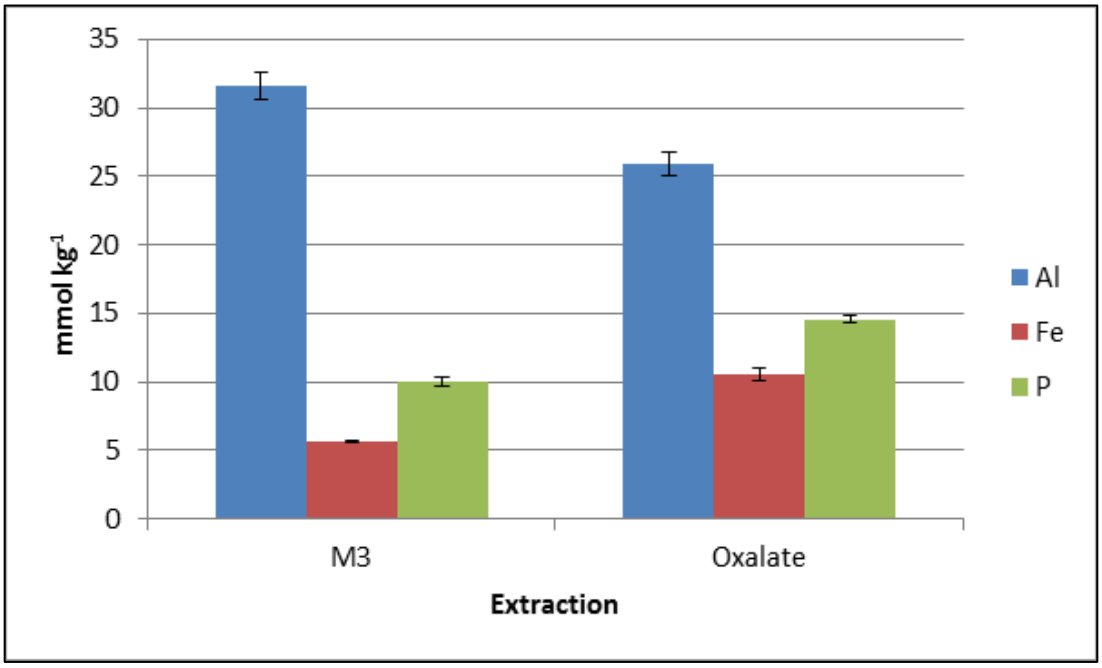


Figure 34. Histogram: Oxalate and M3 Al, P, and Fe

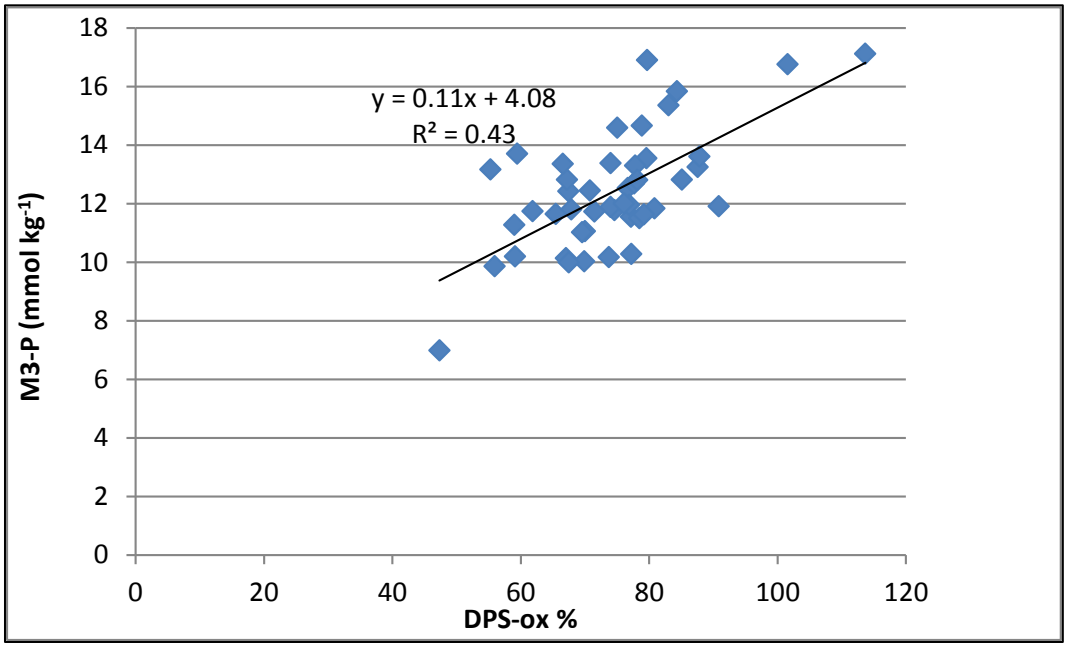


Figure 35. DPSox vs M3-P

A linear relationship was established between DPS_{ox} and M3-PSR ($r^2 = 0.45$, Fig. 36). Sims et al. (2002) found that M3-PSR of 0.10 and 0.15 corresponds to DPS_{ox} 25-40%: the level considered of environmental concern, whereas Maguire and Sims (2002) found M3-PSR of 0.068 to correspond to DPS_{ox} of 25%. According to the linear relationship found here, a M3-PSR of 0.12 – 0.18 corresponds to DPS_{ox} 25-40%.

Several studies have found an abbreviated M3-PSR calculation, that omits Fe_{ox}, can be used and produce nearly identical results (Maguire and Sims, 2002; Sims et al., 2002). Results here corroborate previous findings, demonstrating an almost one-to-one relationship ($r^2 = 0.99$, Fig. 37).

Finally, Kleinman and Sharpley (2007) disregarded the use of the alpha value, finding a high correlation between $Psat_{M3}$ and $Psat_{ox}$ ($r = 0.94$). I did the same and also found a relatively close relationship ($r^2 = 0.72$, Fig. 38).

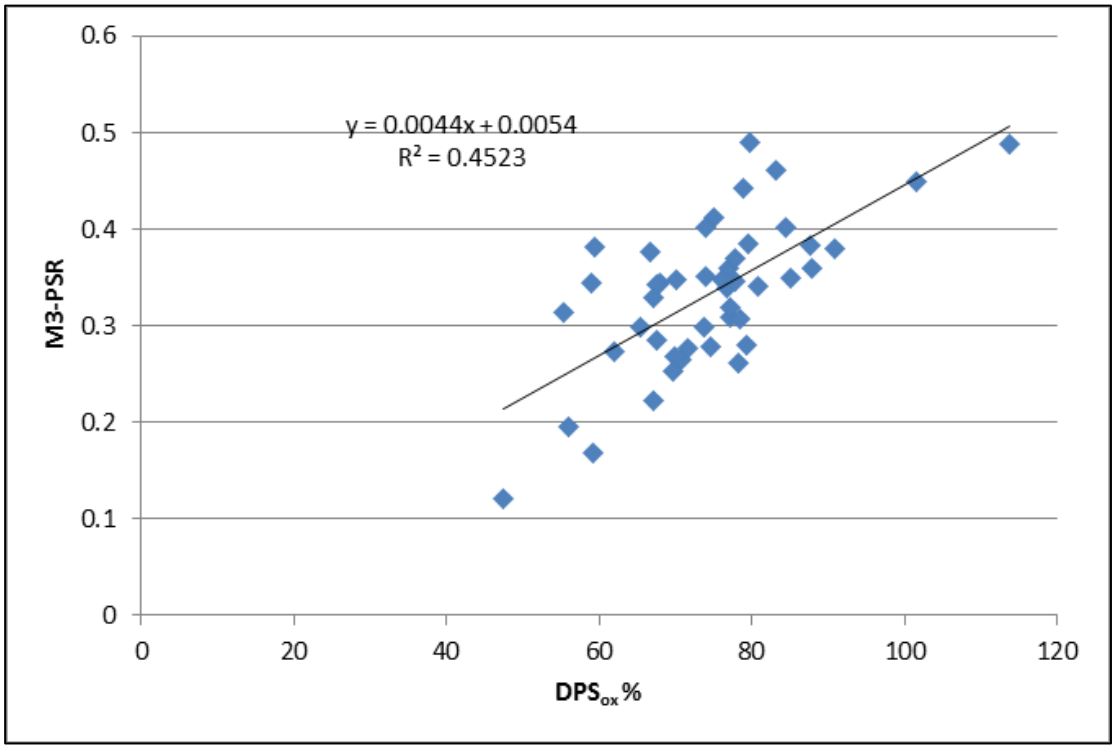


Figure 36. Degree of P Saturation by oxalate extraction vs M3 P Saturation Ratio

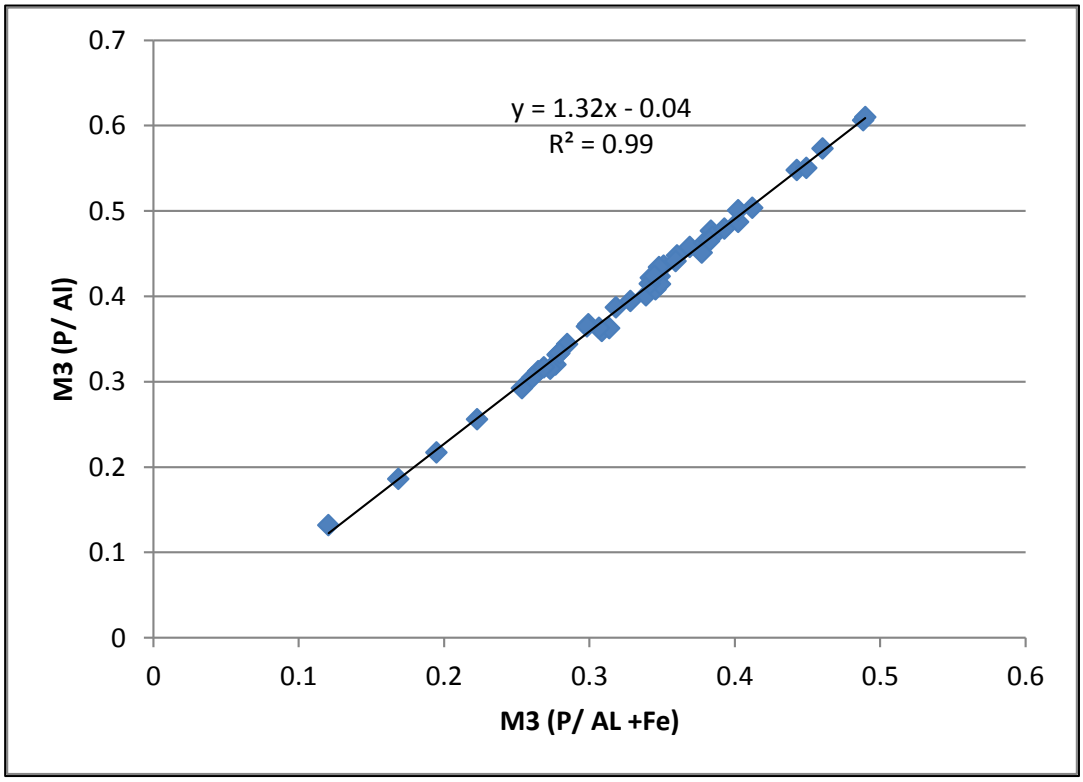


Figure 37. M3-P Saturation Ratio vs. (M3-P/M3-Fe)

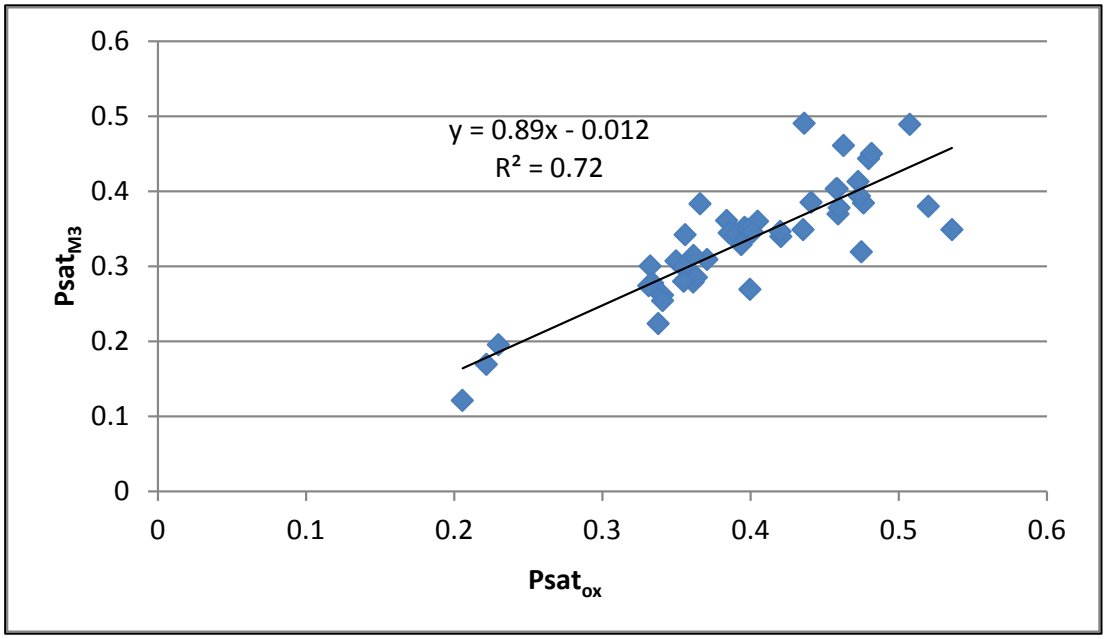


Figure 38. P saturation defined as P/(Al+Fe). Oxalate extraction vs. Mehlich 3 extraction.

Sulfur

Most soil in the U.S. contains 100-600 ppm S (Tabatabai, 1984), and all treatment levels were within this range. There was no significant difference in total S between treatments at the 91 cm (36 in) depth and no discernable pattern in total S at the 61 cm (24 in) depth (Fig. 39). Sulfates applied by gypsum did not travel to these depths. Given the high water table in the field, and the relatively high solubility of most sulfates (Brady and Weil, 2008b), the anion could potentially leach out towards the drainage ditches via subsurface flow, rather than traveling deeper into the soil profile. The data indicates that S reached down to at least 30 cm, deeper than reported by Rhoton and McChesney (2011). Also, these depths are approximate and may actually be deeper due to compaction of the soil cores (Fig. 9 and 10).

Within treatments, significant differences by depth were present among all but the control (Fig. 40), a clear indication of the chemical impact of FGD gypsum on the soil one year after application. Although there was no difference in total S by depth between the 10 and 15 Mg ha^{-1} treatments, total S decreased with depth in both by similar increments. This does not explain the disproportionate S rates across the treatments, however. At the 15 cm, the 10 Mg ha^{-1} treatment sample mean ($\bar{x}$) of 589 mg kg^{-1} S indicated far more S than would be expected when compared to the other treatments at the same depth. The 15 Mg ha^{-1} treatment ($\bar{x}$ = 571 mg kg^{-1} S) had approximately three-fold the amount of total S in the 5 Mg ha^{-1} treatment ($\bar{x}$ = 207 mg kg^{-1} S), which is proportional, but was essentially the same as the 10 Mg ha^{-1} treatment. Perhaps the excess sulfates in the FGD gypsum were easily leached away, due to the slow mineralization of S (Eriksen, 1997). The 5 Mg ha^{-1} treatment was only slightly higher than the control

treatment at the most shallow depths. A soybean crop was planted and harvested between FGD gypsum application and core retrieval, suggesting that perhaps the excess sulfates available were absorbed quickly and easily by the soybean plants. Still, I find it difficult to explain the virtually identical total S data for the two highest treatments.

The FGD gypsum applied contained 3300 mg kg^{-1} sulfate (unpublished data), which translates to 16.5 kg sulfate per hectare at the 5 Mg ha^{-1} level. In a study by Salvagiotti et al. (2012), in which they delivered S in the form of gypsum at rates of at least 15 and 20 kg S ha^{-1}, the S detected in soybean seed was in the range of 11-13 kg ha^{-1}. Seed S contents from the untreated fields was up to 30% less. This research occurred on Mollisols of comparable pH (5.3-5.6) and less sandy textures. I did not perform a soybean plant analysis for this study. Regardless, the study cited above by Salvagiotti et al. (2012) provides some evidence that most of the sulfates applied in the 5 Mg ha^{-1} treatment may have been absorbed by the soybean crop.

Water extraction of Set C samples (taken from the field within a few weeks of the cores and analyzed by USDA-ARS, along with WEP) did clearly indicate relative differences between treatments in regards to water-soluble sulfur (Fig. 41), following a trend that would be expected based on the applied treatments, although there was little difference in sulfur rates between the 10 ($\bar{x}$ = 282 mg kg^{-1}) and 15 Mg ha^{-1} ($\bar{x}$ = 311 mg kg^{-1}) conditions, similar to total S findings. The 5 Mg ha^{-1} treatment level ($\bar{x}$ = 28 mg kg^{-1}) for water-soluble S was one-sixth that of the 10 Mg ha^{-1} treatment. Presumably, water-soluble S would be easily subject to loss and most plant available, which helps to explain the control treatment exhibiting only an average of 4 mg kg^{-1} water-soluble S.

S requirements of legumes, such as soybean, are generally much greater than that of cereals due to their increased concentration of protein and S-containing amino acids (Scherer and Lange, 1996) and soybean yield reduction can usually be attributed to S and P deficiencies due to the N-fixing capacity of soybean (Salvagiotto et al., 2012). Phosphorus deficiencies are clearly not an issue in the field under discussion here. The owner of the field has stated that he has applied S as part of his fertilizer plan in years past. Based on the data here, one could assume that somewhere around 5 Mg ha^{-1} $CaSO_4^{2-}$ is sufficient for the soybean, and therefore sufficient for corn. Without plant analysis, however, this assumption cannot be substantiated.

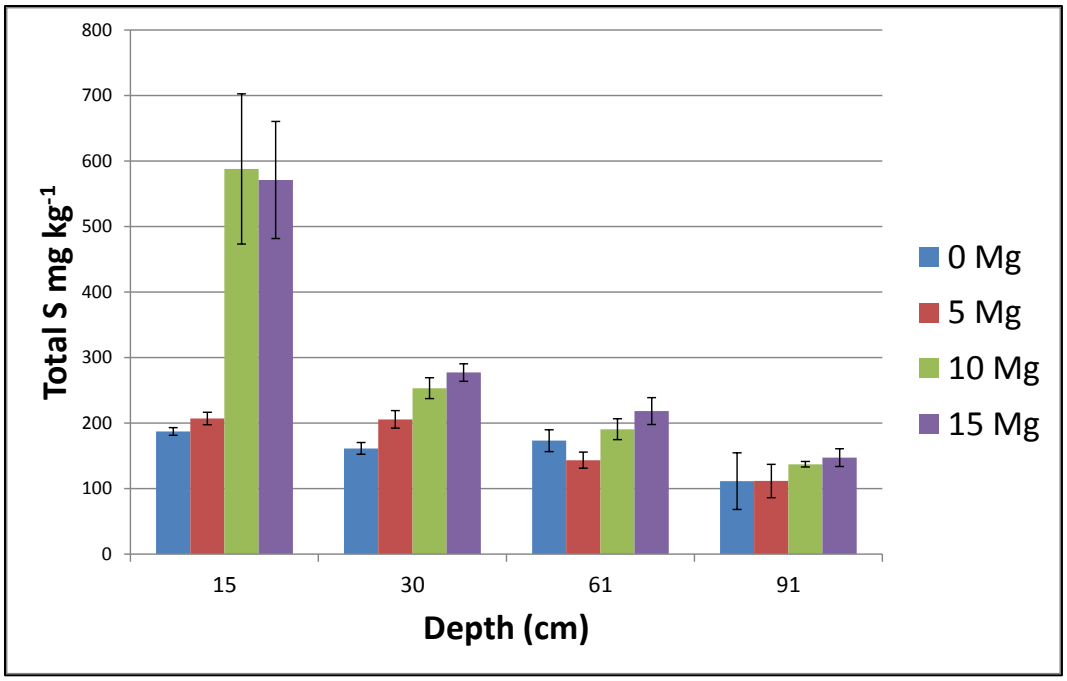


Figure 39. Histogram: Total S by depth

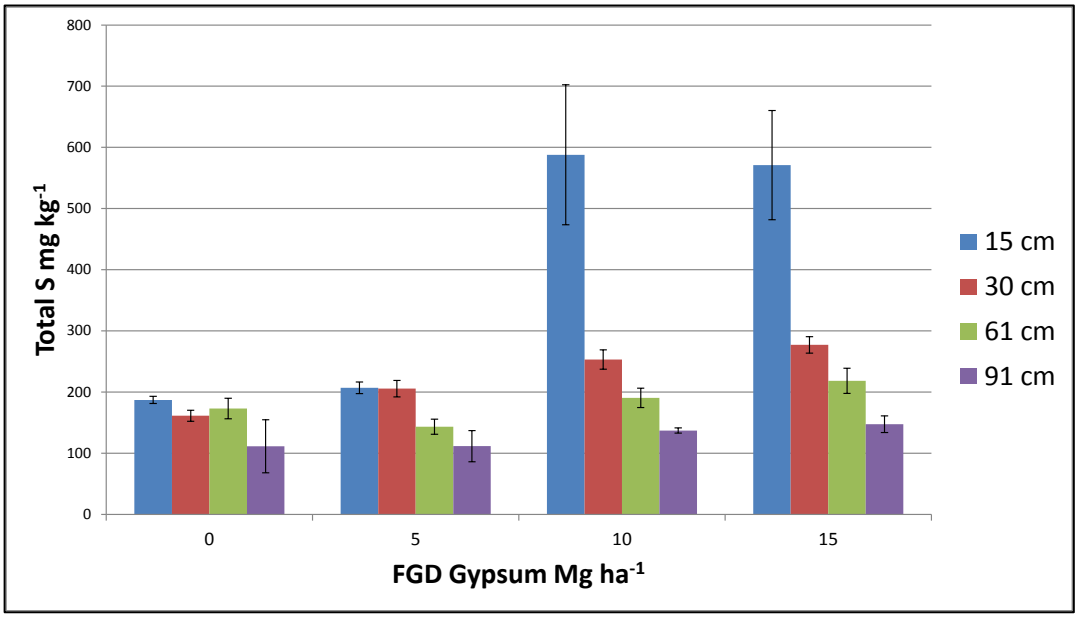


Figure 40. Histogram: Total S by treatment

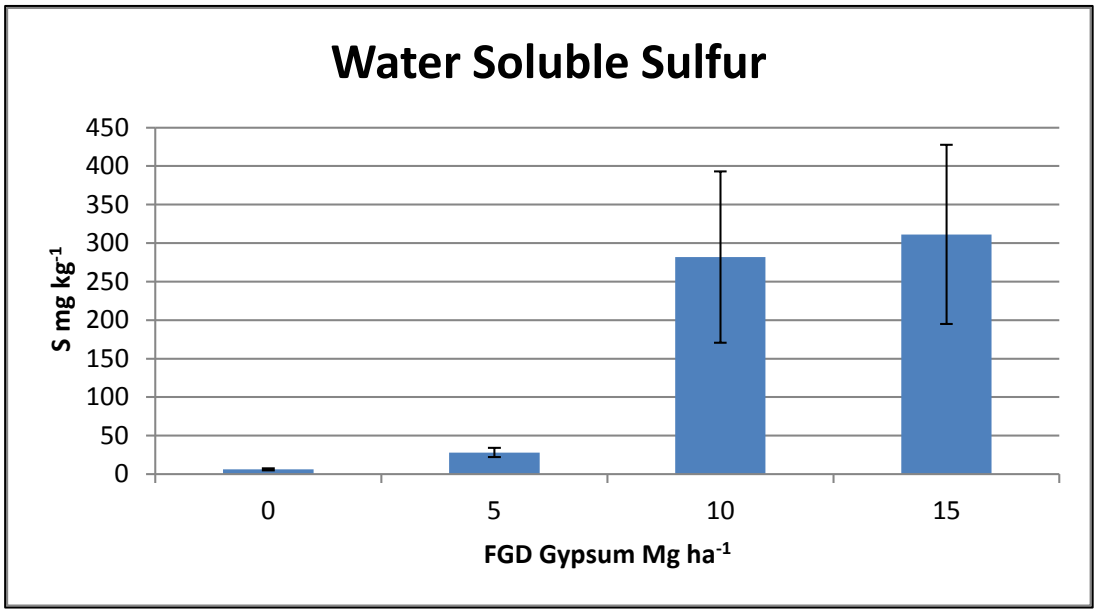


Figure 41. Histogram: Water Soluble S by FGD treatment level one-year after application.

CHAPTER FIVE: CONCLUSIONS AND LIMITATIONS

The main objective of this thesis was to investigate the potential use of FGD gypsum to improve infiltration in a Coastal Plain on the Lower Eastern Shore of Maryland. The benefits of improved infiltration include allowing farmers access to oft water-logged fields with heavy farm machinery earlier in the spring, lessening run-off along the edges of the field, and encouraging sub-surface flow of phosphorus, allowing it to bind with available Al and Fe sites in the soil, or flow towards installed FGD gypsum curtains that would impede the passage of soluble P into drainage ditches. The data here indicated that there may have been a slight improvement in infiltration at the 10 and 15 Mg ha^{-1} application rates, but the effect was fleeting and dissipated within a year. Additionally, there was no relationship between exchangeable Ca and final infiltration rate, which would be expected if FGD gypsum had a direct effect on infiltration rate. Inferences outside the study site cannot be made because the experimental design did not account for extraneous factors in the field. For example, forage radish was planted in the fall immediately prior to FGD gypsum application as a winter cover crop, possibly providing additional root channels in the soil. Care was taken to set the infiltrometer rings between root channels, but it is still possible that infiltration was affected by the radishes. The simple segregated design used for the FGD gypsum application was neither randomized nor replicated, making it easy to conclude there is an effect when there is not; a Type I error (Hulbert, 1984).

Due to the lack of replication, it would have been all the more valuable to have additional data from the field when the infiltration data were collected. Had I to do this again, I would have taken multiple soil samples within each treatment for soil moisture

content and bulk density. Additional difficulty resulted from the use of private land. It is not often easy to find land-owners that are willing to offer land for research, and when they do, the researchers take on some risk simply because they are not in control of management practices. In this case, the farm owner land-leveled the field before two full years of data could be collected. Ironically, the owner felt urgency in leveling the field due to visible indications of variable drainage from ponding around the field, which would have had some effect on infiltration measurements.

Another potential issue in drawing any conclusions from the field study is the manner in which the FGD gypsum was applied, with a manure spinner spreader. This type of application has been shown to lack uniformity across its width, allowing up to one-third of the manure to land directly behind the spreader (University of Maryland Department of Environmental Science and Technology, 2012). This variability can be lessened by multiple off-set passes by the spreader. I do not know if this occurred at the field site and there is no written record of how the FGD gypsum was applied. It is known that the spreader passed over each treatment row once per 5 Mg ha^{-1} rate. This means for the three treated levels of 5, 10, and 15 Mg ha^{-1} FGD gypsum; the manure spreader passed over the respective treatment row 1x, 2x, or 3x. This may have potentially resulted in even greater variability within the treatment rows. Use of exchangeable Ca as a surrogate for the categorical treatment values permitted statistically sound regression analysis, but was not ideal.

A rainfall simulation was conducted in an effort to control for the factors that would have been an issue in the field. The methods were drawn from several studies (Ben-Hur et al., 1992; Miller, 1987; Tang et al., 2006; Warrington et al., 1989) that where

specifically focused on run-off, although they presented the effects of gypsum on infiltration curves. Packing the trays was a complicated task, and uniformity in packing was difficult to ensure or quantify. Also, it would have been far more precise to directly measure infiltration, rather than calculating is by subtracting runoff from estimated total rainfall. Regardless, the lab simulation did not return data showing any discernable trend, and therefore no effect of FGD gypsum on infiltration rate.

It seems clear that FGD gypsum application did temporarily decrease WEP in the soil. I do not have a definitive answer for the temporary nature of the effects. My first thought is that the surge of Ca into the system resulted in a quick precipitation of calcium phosphate that was eventually solubilized and dissipated due to the acidity of the soil. A larger sample size would likely have provided more definitive evidence of this and certainly would have helped in examining the interactions between water, M3 and ammonium oxalate extractions, and P sorption isotherms. Generally the relationships between methods agreed with what is available in the literature--reiterating the usefulness of M3 in both agronomic and environmental analysis.

There was a clear increase in total S at surface depths a year after FGD gypsum application, although no change at depths below 30 cm was observed. Ironically, the increased need for sulfur to ensure crop vigor is well-correlated with the reduction in SO_2 resulting from air quality regulations. Applying the by-product of these regulations to return sulfur to the soil seems a rational course of action.

CHAPTER SIX: FUTURE RESEARCH

The supply of FGD gypsum is expected to be steady for some time, thus finding a practical use for it is necessary. It may not be as effective in increasing infiltration on the Coastal Plain as it is in more arid regions of the country, but the observations here indicate that there may be a temporary effect at application rates that are much higher than typical of gypsum use in other regions of the United States. Researchers are currently having success using FGD gypsum in drainage ditches to precipitate and trap phosphates (McGrath, 2013). The advantage of surface application is the simultaneous application of sulfur for fertilization purposes. A larger sample set within a well-planned experimental design may be worth initiating to get a better scope of the true effects of FGD gypsum on infiltration, phosphorus, and sulfur on these heavily manured soils. A soil column study, with either intact columns from an un-treated part of the cultivated field or packed in the lab to a depth that would have allowed for a wetting front to form would provide a better measure of infiltration. There is always a need for more field data, as well. A randomized, multiple field study would be ideal. Between FGD application and the land-leveling of the field, one planting and harvesting of soybean occurred. It would have been quite useful to have specimens from the field for analysis of plant S. A plant analysis could provide a clearer picture of the fate of the sulfate that is applied.

APPENDICES

Appendix 1. List of Equations

Equation 1	% Degree of P Saturation	$\frac{Pox}{\alpha\ (Alox + Feox)} * 100$
Equation 2	Phosphorus Saturation Ratio	$\frac{M3P}{M3Al + M3Fe}$
Equation 3	P sorption saturation	$\frac{Sorbed\ P}{P\ sorption\ capacity}$
Equation 4	Langmuir	$S = \frac{SmaxKC}{1 + KC}$
Equation 5	Freundlich	$S = K_f C^n$
Equation 6	Philip Equation for Cumulative Infiltration	$I(t) = St^{1/2} + At$
Equation 7	Philip's Derivative for Infiltration Rate	$i = \frac{1}{2} St^{-\frac{1}{2}} + A$
Equation 8	Darcy's velocity	$q = \frac{Q}{A \cdot t}$
Equation 9	Saturated Conductivity	$K_{sat} = q \cdot \frac{\Delta z}{\Delta h}$
Equation 10	Alpha Value	$\propto = \frac{P_{ox} + S_{max}}{Al_{ox} + Fe_{ox}}$

Appendix 2. Soil Core Profiles

Aa #1 (deep)					Aa #2					Aa #3					Aa #4				
Horizon[1]	**Depth[2] (cm)**	**Color[3]**	**Texture[4]**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	22	2.5Y 3/1	L		**Ap**	19	2.5Y 3/1	L		**Ap**	13	2.5Y 3/1	L		**Ap**	22	2.5Y 4/1	SL	
Btg	35	2.5Y 4/1	CL	x	**Btg**	60	2.5Y 4/1	C	x	**Ap2**	26	10YR 3/1	L		**Btg**	40	2.5Y 5/1	SC	x
Btg2	50	2.5Y 4/1	CL/C	x	**Btg2**	80	2.5Y 4/1	SCL	x	**Btg**	50	10YR 4/1	C	x	**Btg2**	50	2.5Y 4/1	SC/C	x
Btg3	64	2.5Y 4/1	SCL	x	**CBg**	86	2.5Y 5/2	SL	x	**BCg**	61	10YR 4/1	SL/SCL	x	**Btg3**	63	2.5Y 4/1	SCL	x
C/Bg	102	2.5Y 4/1	LS	x						**Cg**	76	10YR 5/2	LS/S	x	**CBg**	85	2.5Y 4/1	SL	x
C	111	10YR 5/4	LS	x															
2C	150	2.5Y 5/3	L	x															
3C	172	2.5Y 5/2	LS	x															
Ba #1 (deep)					**Ba #2**					**Ba #3**					**Ba #4**				
Horizon[1]	**Depth[2] (cm)**	**Color[3]**	**Texture[4]**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	26	10YR 3/1	L		**Ap**	22	2.5Y 3/1	L		**Ap**	25	2.5Y 3/1	L		**Ap**	22	10YR 3/1	L	
Btg	54	10YR 5/1	CL	x	**Btg**	45	2.5Y 5/1	SCL	x	**Btg**	52	2.5Y 4/1	C	x	**Btg**	48	2.5Y 4.5/1	SCL	x
Cg	97	2.5YR 3/1	LS	x	**CBg**	64	2.5Y 5/1	LS		**CBg**	62	2.5Y 4/1	SL	x	**Cg**	62	2.5Y 4/1	LS	
2Cg	132	2.5YR 5/1	LS	x	**Cg2**	78	2.5Y 6/1	S/LS	x	**Cg**	79	2.5Y 5/2	LS	x	**2Cg**	83	2.5Y 5.5/2	LS/S	x
3Cg	147	2.5YR 6/1	L	x															

1-Taxonomic Classification codes based on USDA-NRCS system. For specific coding information see Schoeneberger, P.J., D.A. Wysocki, E.C. Benham, and Soil Survey Staff. 2012. Field book for describing and sampling soils, Version 3.0. Natural Resources Conservation Service, National Soil Survey Center, Lincoln, NE.

2-Number reflects lower boundary of the horizon. Lowest depth is bottom of core, not necessarily bottom of horizon.

3-Munsell Color System coding

4-L=Loam; C= Clay; S= Sand

Appendix 2.2 Soil Core Profiles

Ca #1 (deep)					Ca #2					Ca #3					Ca #4				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	20	2.5Y 4/2	L		**Ap**	23	2.5Y 3/1	SL		**Ap**	20	2.5Y 3/1	L		**Ap**	22	2.5Y 4/1	L	
Btg	36	2.5Y 5/1	CL/C	x	**Btg**	45	2.5Y 5/1	CL	x	**Btg**	46	2.5Y 4/1	CL	x	**Btg**	63	2.5Y 5/1	C	x
Btg2	49	2.5Y 5/1	SCL	x	**Cg**	66	10YR 5/1	LS	x	**CBg**	63	2.5Y 4/1	LS	x	**Cg**	82	2.5Y 5/2	S	x
CBg	73	2.5Y 5/1	LS	x	**2C**	82	2.5Y 5/3	S		**Cg**	80	10YR 6/2	S		**2Cg**	86	2.5Y 6/2	LS	x
Cg	78	2.5Y 6/2	S																
2Cg	91	2.5Y 5/1	LS	x															
3Cg	118	2.5Y 4/2	S	x															
4Cg	151	2.5Y 4/2	LS	x															
5Cg	156	10 YR 5/6	FSL	x															
Da #1 (deep)					**Da #2**					**Da #3**					**Da #4**				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	22	10YR 3/1	L		**Ap**	19	2.5Y 3/1	L		**Ap**	21	10YR 3/1	L		**Ap**	24	10YR 3/1	L	
EB	34	10YR 5/1	L	x	**Btg**	52	2.5Y 4.5/1	C	x	**Btg**	31	2.5Y 4/1	CL/C	x	**Btg**	60	2.5Y 4/1	CL	x
Bg	51	2.5Y 5/2	CL	x	**CBg**	71	2.5Y 4/1	LS	x	**Btg2**	55	2.5Y 5/2	CL	x	**CBg**	72	2.5Y 4/1	SL	x
Cg	84	2.5Y 4/1	LS	x	**Cg**	80	2.5Y 4/2	LS/S	x	**CBg**	78	10YR 4/2	LS	x	**Cg**	84	2.5Y 4/1	LS/S	
2Cg	104	2.5Y 5/2	LS	x						**Cg**	82	2.5Y 4/2	S		**2Cg**	88	2.5Y 5/2	SL	
3Cg	121	2.5Y 6/2	LS	x															
4Cg	149	2.5Y 6/2	SL	x															
5Cg	156	2.5Y 5/2	SCL	x															

Appendix 2.3 Soil Core Profiles

Ab #1 (deep)					**Ab #2**					**Ab #3**					**Ab #4**				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	20	2.5Y 5/1	L		**Ap**	18	10YR 3/2	L		**Ap**	18	2.5Y 3/1	L		**Ap**	20	10YR 3/2	SL	
Btg	42	2.5Y 5/1	CL	x	**BEg**	24	10YR 5/1	L	x	**Btg**	52	2.5Y 5/1	C	x	**Btg**	42	2.5Y 4/1	CL	x
CBg	69	2.5Y 5/1	LS/SL	x	**Btg**	37	2.5Y 5/1	L/CL	x	**CBg**	82	2.5Y 4/1	LS/SL	x	**Btg2**	58	2.5Y 5/1	SCL	x
Cg	89	2.5Y 5/1	LS/SL	x	**Btg2**	47	2.5Y 5/1	SL/SCL	x	**Cg**	87	2.5Y 5/2	S		**Cg**	80	10YR 4/1	LS	x
2Cg	128	2.5Y 5/1	LS/S	x	**Btg3**	68	10YR 5/1	SL	x										
3C	138	2.5Y 5/1	LS	x	**2Cg**	90	2.5Y 6/1	S	x										
Bb #1 (deep)					**Bb #2**					**Bb #3**					**Bb #4**				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	16	10YR 3/1	L		**Ap**	18	10YR 3/1	L		**Ap**	19	2.5Y 3/1	L		**Ap**	14	2.5Y 3/2	L	
EB	23	10YR 4/1	L		**Btg**	42	2.5Y 5/1	CL	x	**Btg**	53	2.5Y 4/1	CL	x	**EB**	19	2.5Y 3/2	SCL	
Btg	70	2.5Y 5/1	CL	x	**Btg2**	69	10YR 4/1	CL	x	**Btg2**	74	10YR 4/1	SCL	x	**Btg**	40	2.5Y 5/1	SCL/SC	x
BCg	91	2.5Y 4/1	SL	x	**Cg**	82	2.5Y 5/1	LS		**Cg**	84	10YR 4/1	SL	x	**Btg2**	62	2.5Y 5/1	CL/L	x
Cg	132	2.5Y 6/2	LS	x											**CBg**	72	10YR 5/1	SL	x
2Cg	143	2.5Y 5/2	SL	x											**Cg**	80	2.5Y 5/1	LS	x

Appendix 2.4 Soil Core Profiles

Cb #1 (deep)					**Cb #2**					**Cb #3**					**Cb #4**				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	20	10YR 3/1	L		**Ap**	21	10YR 3/1	L		**Ap**	25	2.5Y 3/1	L		**Ap**	24	10YR 3/1	L	
AE	26	10YR 4/1	L/SL		**BEg**	25.5	10YR 3/1	SL		**BEg**	31	2.5Y 4/1	SCL	x	**Btg**	62	2.5Y 5/1	CL/C	x
Btg	40	2.5Y 5/2	SC	x	**Btg**	53	2.5Y 4/1	SCL/SC	x	**Btg**	60	10YR 4/1	C	x	**Btg2**	78	2.5Y 5/1	SCL	x
BCg	70	2.5Y 5/1	LS	x	**Btg2**	63	2.5Y 5/1	SCL	x	**Cg**	79	2.5Y 4/2	LS	x	**Cg**	84	2.5Y 5/1	LS	
CB	112	2.5Y 6/4	S/LS	x	**BCg**	70	2.5Y 4/1	SL	x										
C	114	2.5Y 5/4	LS	x	**CBg**	85	2.5Y 5/1	LS	x										
2C	153	2.5Y 5/2	LS/SL	x															
Db #1 (deep)					**Db #2**					**Db #3- High Organic Matter in A horizon**					**Db #4**				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	26	10YR 3/1	L		**Ap**	18	10YR 4/1	L		**Ap**	23	10YR 3/1	L		**Ap**	33	10YR 3/1	L	
Btg	59	2.5Y 4/1	CL	x	**AEg**	27	10YR 4/1	L/SL		**Ab**	45	10YR 2/1	L		**Btg**	50	10YR 4/1	C	x
Cg	80	2.5Y 4/1	LS	x	**Btg**	69	2.5Y 4/1	SCL	x	**Btg**	74	2.5Y 4/2	CL/C	x	**Cg**	83	10YR 5/1	LS	x
2Cg	107	2.5Y 6/2	LS		**BCg**	79	2.5Y 5/1	LS	x	**BCg**	81	2.5Y 4/1	SL/SCL	x					
3C	138	2.5Y 5/4	LS	x	**Cg**	81	10YR 4/1	LS	x										
4C	156	2.5Y 6/2	LS/SL	x															

Appendix 2.5 Soil Core Profiles

Ac #1 (deep)					**Ac #2**					**Ac #3**					**Ac #4**				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	20	10YR 3/1	SL		**Ap**	22	10YR 3/1	L		**Ap**	25	10YR 3/1	L/SL		**Ap**	20	2.5Y 3/2	L	
Btg	54	2.5Y 4/2	SCL	x	**BA**	32	5Y 3/1	CL		**Beg**	33	2.5Y 4/1	SL		**BEg**	30	10YR 4/2	CL	
Cg	123	2.5Y 5/2	LS	x	**Btg**	50	10YR 4/1	CL	x	**Btg**	66	10YR 4/1	SC	x	**Btg**	44	2.5Y 4/1	CL	x
Cg2	161	2.5Y 6/2	SL	x	**Btg2**	61	10YR 4/1	SCL	x	**CBg**	78	10YR 5/1	SL	x	**Btg1**	69	2.5Y 5/1	SCL	x
					Cg	76	2.5Y 4/1	LS	x						**Cg**	76	2.5Y 4/2	S/LS	x
Bc #1 (deep)					**Bc #2**					**Bc #3**					**Bc - High Organic Matter in BE horizon**				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	20	10YR 3/1	L		**Ap**	20	10YR 3/1	L		**Ap**	22	10YR 3/2	L		**Ap**	24	2.5Y 4/1	SL	
Btg	48	2.5Y 4/1	SCL/CL	x	**Btg**	29	2.5Y 5/1	C/CL	x	**Btg**	41	2.5Y 4/1	CL	x	**BEg**	30	2.5Y 4/1	SCL	x
CBg	65	2.5Y 4/1	LS/SL	x	**Btg2**	44	2.5Y 5/1	SCL	x	**Btg2**	58	2.5Y 5/1	SCL	x	**Btg**	54	2.5Y 5/1	SCL	x
Cg	79	2.5Y 6/2	FS		**Cg**	80	2.5Y 4/2	LS	x	**Cg**	75	2.5Y 5/1	LS		**CBg**	70	2.5Y 5/1	SL	
2C	92	10YR 3/2	L												**Cg**	82	2.5Y 5/2	S	
3C	118	2.5Y 5/3	SCL/CL																
4C	141	10YR 5/6	FLS	x															
5C	147	2.5Y 6/2	FSL	x															

Appendix 2.6 Soil Core Profiles

Cc #1 (deep)					Cc #2					Cc #3-High Organic Matter and Charcoal in EB and B horizon					Cc #4				
Horizon[1]	**Depth[2] (cm)**	**Color[3]**	**Texture[4]**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	28	10YR 3/1	L		**Ap**	26	2.5Y 3/1	L		**Ap**	26	10YR 3/1	L		**Ap**	25	10YR 3/1	L	
Btg	65	2.5Y 4/1	CL/SCL	x	**EBg**	35	10YR 5/1	L	x	**Ebg**	36	2.5Y 4/1	SCL	x	**Btg**	52	10YR 5/1	CL	x
CBg	89	2.5Y 4/2	LS/SL	x	**Bg**	42	2.5Y 4/1	SL	x	**Btg**	80	2.5Y 5/1	SCL/CL	x	**Btg2**	65	10YR 4/1	SCL	x
Cg	134	2.5Y 6/2	S	x	**Bg**	65	10YR 4/1	SL/LS	x						**CBg**	89	2.5Y 4/1	LS	x
2Cg	147	2.5Y 6/1	FSL	x	**Btg**	84	2.5Y 4/1	SC/SCL	x										
					BCg	90	10YR 4/1	SL/LS	x										
Dc #1 (deep)					**Dc #2**					**Dc #3**					**Dc #4**				
Horizon[1]	**Depth[2] (cm)**	**Color[3]**	**Texture[4]**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	22	10YR 3/1	L		**Ap**	17	10YR 3/1	SL		**Ap**	21	10YR 3/1	L		**Ap**	25	10YR 3/1	SL	
Btg	78	2.5Y 4/1	SCL	x	**BEg**	28	2.5Y 4/1	SCL		**EBg**	28	2.5Y 4/1	L/SL		**EBg**	32	2.5Y 4/1	SL	x
CB	103	2.5Y 4/1	CoSL	x	**Btg**	56	2.5Y 4/1	C/SiC	x	**Btg**	62	10YR 5/1	CL	x	**Btg**	68	2.5Y 4/1	C	x
C	131	2.5Y 6/4	LS		**BC**	82	2.5Y 4/1	SCL	x	**Cg**	82	2.5Y 4.5/1	SL	x	**Cg**	81	10YR 4.5/1	LS	x
2C	149	2.5Y 6/2	FSL	x															

Appendix 2.7 Soil Core Profiles

Ad #1 (deep)					**Ad #2- BA horizon high in organic matter**					**Ad #3**					**Ad #4**				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	22	10YR 3/1	L		**Ap**	19	2.5Y 3/1	SL		**Ap**	17	10YR 3/1	L		**Ap**	21	2.5Y 3/1	L	
Btg	56	2.5Y 4/2	CL	x	**BA**	28	2.5Y 4/1	CL	x	**Bt**	35	10YR 4/4	C/SC	x	**Btg**	35	2.5Y 4/1	CL/SCL	x
BCg	86	2.5Y 4/2	SL	x	**Btg**	43	2.5Y 5/1	SCl	x	**Btg**	51	10YR 4/1	SCL	x	**Btg**	45	2.5Y 5/1	SCL/CL	x
CBg	98	2.5Y 4/2	SCL	x	**Cg**	74	2.5Y 5/2	LS	x	**Btg2**	68	10YR 4/1	SCL/SC	x	**CBg**	64	2.5Y 4.5/1	SL	x
Cg	124	2.5Y 5/2	SL	x						**Cg**	71	10YR 4/1	LS	x	**Cg**	78	2.5Y 5/1	LS	x
2Cg	160	2.5Y 5/2	LS	x															
3Cg	180	2.5Y 6/1	C/SC	x															
Bd #1 (deep)					**Bd #2- High organic matter in BE horizon**					**Bd #3**					**Bd #4-Substantial amount of charcoal in B horizons.**				
Horizon[1]	**Depth**[2] **(cm)**	**Color**[3]	**Texture**[4]	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	27	10YR 3/1	L		**Ap**	21	2.5Y 5/2	SL		**Ap**	23	2.5Y 3/1	SL		**Ap**	26	2.5Y 3/1	L	
Bt	46	2.5Y 3/1	CL		**BEg**	30	10YR 3/1	SCL	x	**Btg**	36	2.5Y 4/1	SCL	x	**A/Bt**	31	10YR 3/1	L/CL	
Btg	56	2.5Y 4/2	CL/C	x	**Btg**	51	2.5Y 5/2	SC	x	**Btg2**	46	2.5Y 5/1	SL	x	**Btg**	41	10YR 3/1	L	
Btg2	93	2.5Y 4/2	SCL	x	**BCg**	73	2.5Y 5/2	LS	x	**BCg**	60	2.5Y 5/1	SL/LS	x	**Btg**	65	2.5Y 5/2	SL/SCL	x
BC	135	2.5Y 5/3	FLS	x						**CBg**	73	2.5Y 4/1	SL/LS		**CBg**	77	2.5Y 4/1	SL	x
Cg	148	2.5Y 5/2	FSL	x						**Cg**	79	2.5Y 6/2	S						

Appendix 2.8 Soil Core Profiles

Cd #1 (deep)					Cd #2- Very dense region 55-59 cm					Cd #3- EB horizon very dense, high in organic matter					Cd #4-high charcoal, organic matter throughout, gooey, tacky texture				
Horizon[1]	**Depth[2] (cm)**	**Color[3]**	**Texture[4]**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	28	10YR 3/1	L		**Ap**	29	10YR 3/1	L		**Ap**	23	2.5Y 3/1	L		**Ap**	27	10YR 3/1	L	
Bt	44	2.5Y 4/2	CL		**Eg**	34	2.5Y 4/1	SL		**EBg**	31	2.5Y 4/1	CL	x	**Btg**	66	2.5Y 5/1	CL	x
Btg	69	2.5Y 4/1	SC	x	**Btg**	71	2.5Y 4/1	SCL	x	**Btg**	66	2.5Y 4/1	C	x					
BCg	90	2.5Y 4/1	SL	x						**BCg**	71	2.5Y 4/1	SCL	x					
Cg	124	2.5Y 5/2	SL	x															
C	146	2.5Y 5/4	FSL/LS	x															
Dd #1 (deep)- Dominated by charcoal throughout					**Dd #2- High organic matter in BE horizon**					**Dd #3- gooey, tacky texture in Btg horizon**					**Dd #4- high in charcoal, gooey textures**				
Horizon[1]	**Depth[2] (cm)**	**Color[3]**	**Texture[4]**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**	**Horizon**	**Depth (cm)**	**Color**	**Texture**	**Redox**
Ap	26	10YR 3/1	L		**Ap**	28	2.5Y 4/2	L/SL		**Ap**	29	10YR 3/1	L		**Ap**	30	10YR 3/1	L	
Btg	105	2.5Y 4/2	CL	x	**BEg**	35	10YR 5/1	SCL		**BEg**	40	10YR 4/1	CL	x	**Eg**	36	2.5Y 4/1	L	
Btg2	141	2.5 4/1	CL	x	**Btg**	56	2.5Y 5/1	SCL	x	**Btg**	86	2.5Y 4/1	C	x	**Btg**	73	10YR 4/1	C	x
Btg3		2.5 4/1	SCL	x	**Btg2**	80	10YR 3/1	CL/SCL	x	**CBg**	90	2.5Y 4/1	SCL						
					BCg	87	2.5Y 4/2	SCL	x										

Appendix 3. pH & EC Values

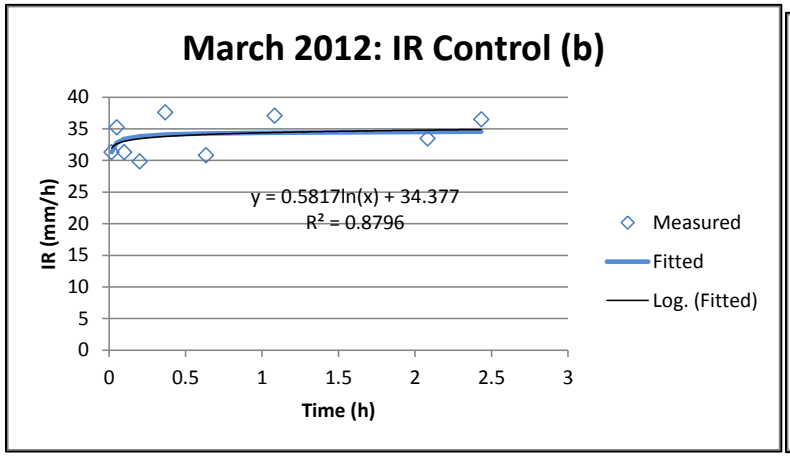
Season	FGD gypsum	Row	pH_w	EC	Season	FGD gypsum	Row	pH	EC
	Mg ha^{-1}			dS m^{-1}		Mg ha^{-1}			dS m^{-1}
Nov '12	0	a	5.2	0.21	**May '13**	0	a	5.2	0.17
Nov '12	0	b	5.5	0.21	**May '13**	0	b	5.4	0.21
Nov '12	0	c	5.4	0.22	**May '13**	0	c	5.2	0.19
Nov '12	0	d	5.3	0.24	**May '13**	0	d	5.1	0.23
Nov '12	5	a		0.30	**May '13**	5	a	5.3	0.30
Nov '12	5	b	5.5	0.29	**May '13**	5	b	5.5	0.18
Nov '12	5	c		0.23	**May '13**	5	c	5.6	0.22
Nov '12	5	d	5.3	0.38	**May '13**	5	d	5.3	0.65
Nov '12	10	a	5.3	0.36	**May '13**	10	a	5.4	0.34
Nov '12	10	b	5.4	0.54	**May '13**	10	b	5.5	0.28
Nov '12	10	c	5.3	0.38	**May '13**	10	c	5.5	0.72
Nov '12	10	d	5.1	0.85	**May '13**	10	d	5	0.83
Nov '12	15	a	5.1	0.70	**May '13**	15	a	5.2	0.64
Nov '12	15	b	5.3	0.42	**May '13**	15	b	5.3	0.93
Nov '12	15	c	5.2	0.86	**May '13**	15	c	5.2	0.80
Nov '12	15	c2	5.4	NA	**May '13**	15	d	5.4	0.30
Nov '12	15	d	5.2	0.31					
March '13	0	a	5.1	0.21					
March '13	0	b	5.4	0.21					
March '13	0	c	5.3	0.20					
March '13	0	d	5.3	0.20					
March '13	5	a	5.2	0.30					
March '13	5	b	5.3	0.29					
March '13	5	c	5.1	0.23					
March '13	5	d	5.1	0.38					
March '13	10	a	5.3	0.36					
March '13	10	b	5.3	0.54					
March '13	10	c	5.5	0.38					
March '13	10	d	4.7	0.85					
March '13	15	a	5.2	0.70					
March '13	15	b	5.2	0.42					
March '13	15	c	5.3	0.86					
March '13	15	d	5	0.31					

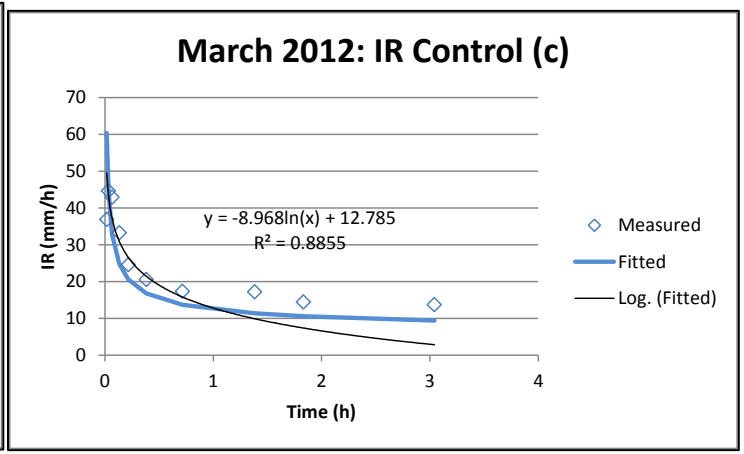
Appendix 4. Philip Equation Parameters

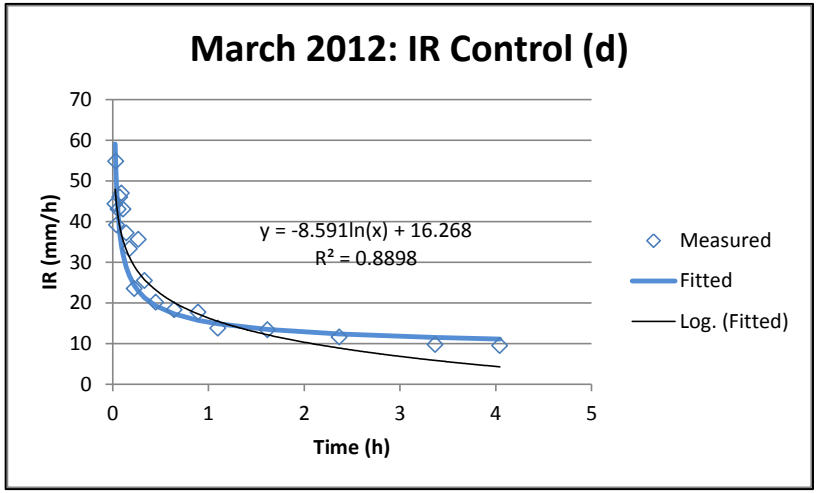
	Mar-12		Nov-12		May-13	
	S	**A**	**S**	**A**	**S**	**A**
Control	N/A	N/A	N/A	N/A	33.03	4.48
	0.00	34.61	18.24	57.95	35.86	26.07
	14.22	5.28	40.45	37.68	16.39	6.15
	16.47	6.98	12.85	54.35	32.80	5.30
Mean	10.23	15.62	23.84	49.99	29.52	10.50
5 Mg ha^{-1}	3.79	8.38	6.93	39.01	43.38	12.07
	N/A	N/A	17.23	35.95	34.93	28.38
	30.84	0.00	N/A	N/A	26.46	19.29
	4.83	10.52	16.02	14.58	20.98	0.00
Mean	13.15	6.30	13.39	29.85	31.44	14.94
10 Mg ha^{-1}	4.25	5.64	9.31	24.28	26.60	0.00
	7.77	1.00	17.52	47.94	9.64	22.35
	6.96	6.33	39.20	33.57	31.16	2.88
	N/A	N/A	11.99	39.52	15.52	1.48
Mean	6.33	4.32	19.50	36.33	20.73	6.68
15 Mg ha^{-1}	2.30	8.77	N/A	N/A	26.12	14.64
	3.77	24.18	83.86	22.63	21.46	28.33
	8.84	0.00	24.26	87.13	5.54	14.58
	0.00	38.29	29.75	102.25	19.15	9.74
Mean	3.73	17.81	45.96	70.67	18.07	16.82

S = sorptivity
A = transmissivity

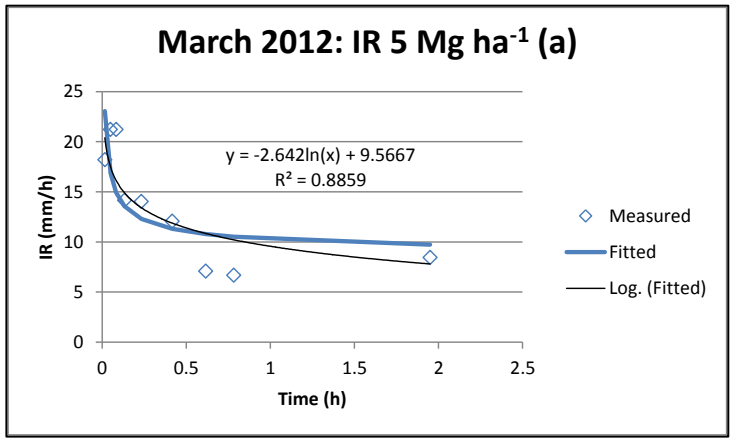
Appendix 5. Infiltration Rate Curves for March 2012, 2 months following FGD gypsum application: 0 Mg ha^{-1}

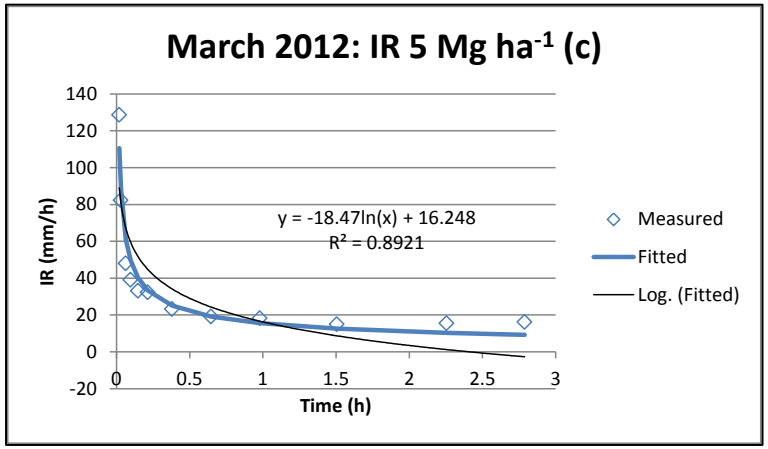


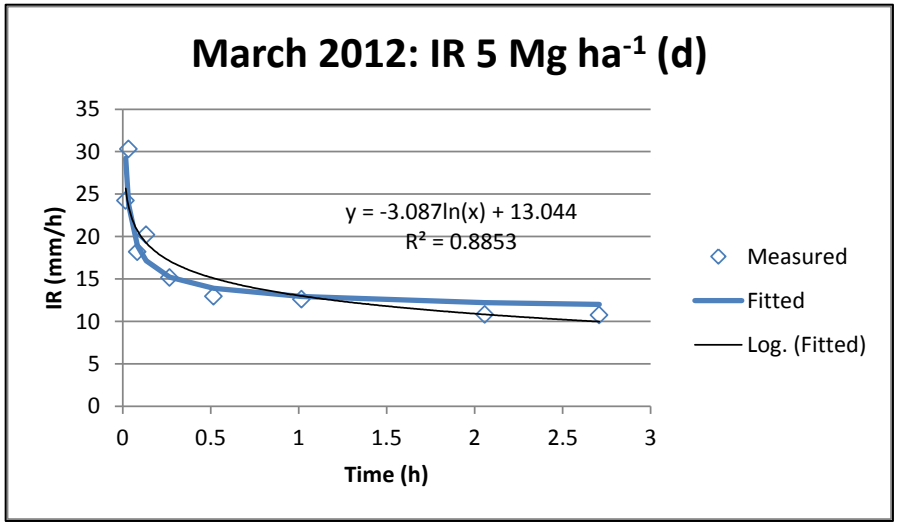




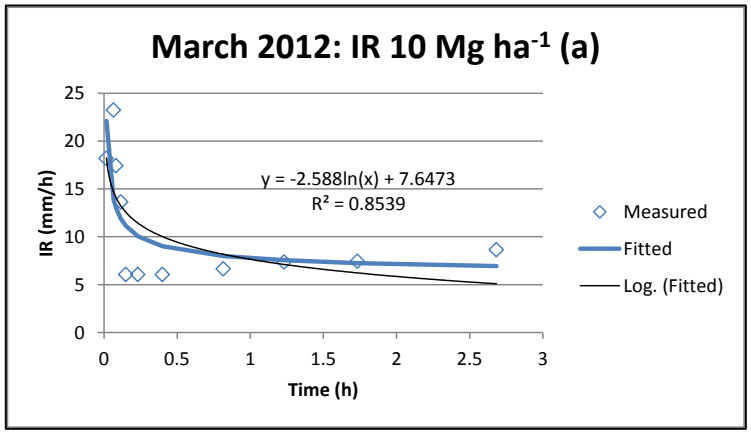
Appendix 5.2. Infiltration Rate Curves for March 2012, 2 months following FGD gypsum application: 5 Mg ha^{-1}

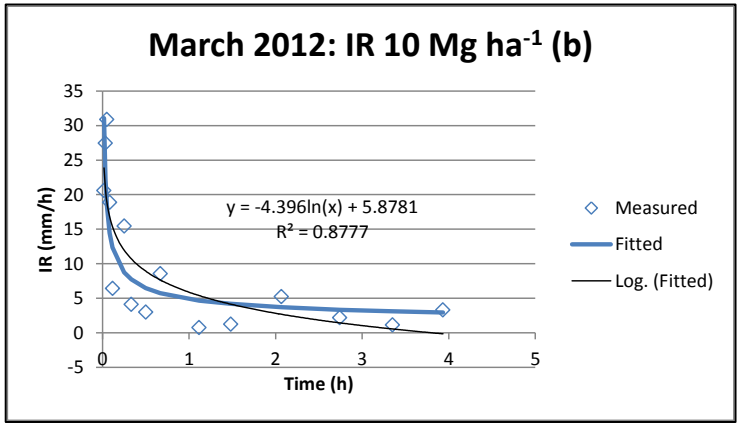


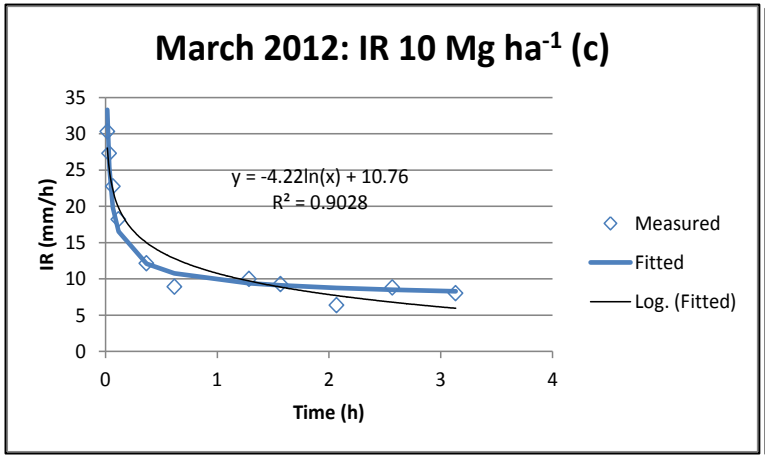


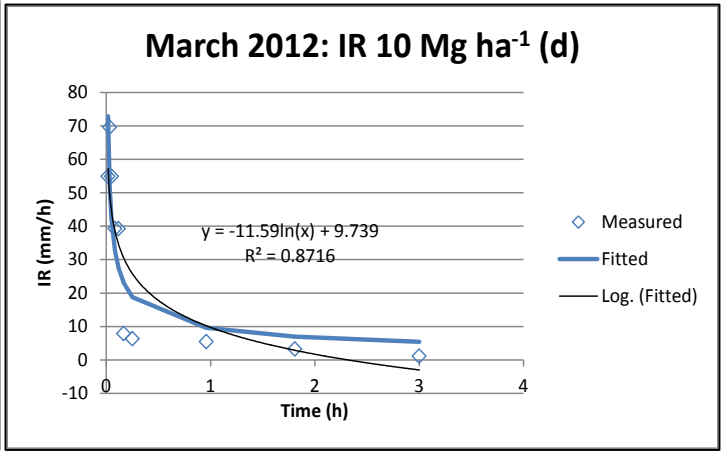


Appendix 5.3. Infiltration Rate Curves for March 2012, 2 months following FGD gypsum application: 10 Mg ha^{-1}

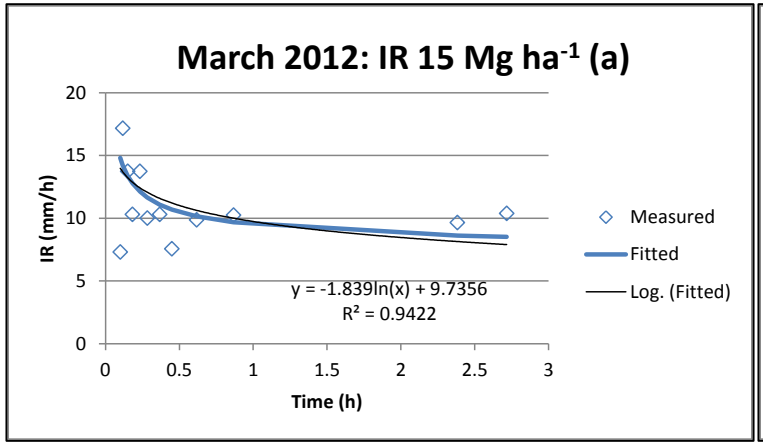


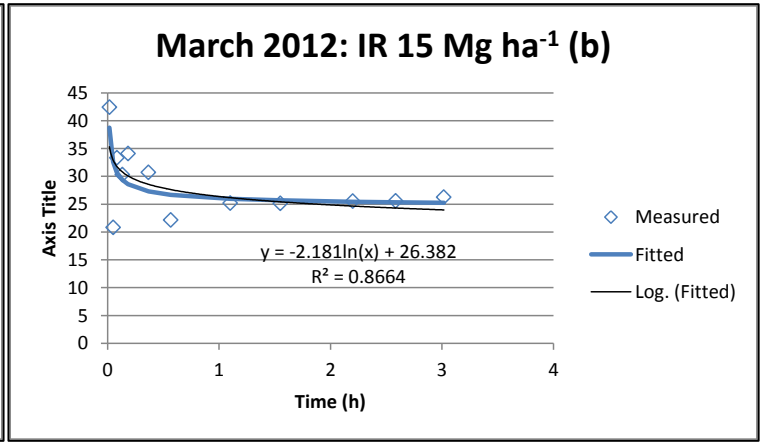


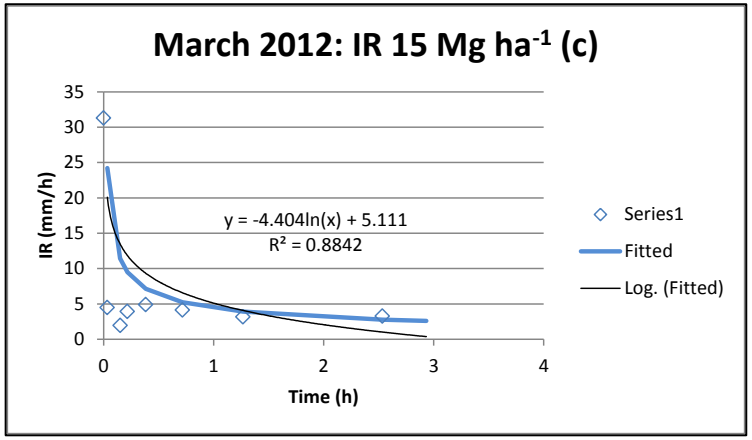


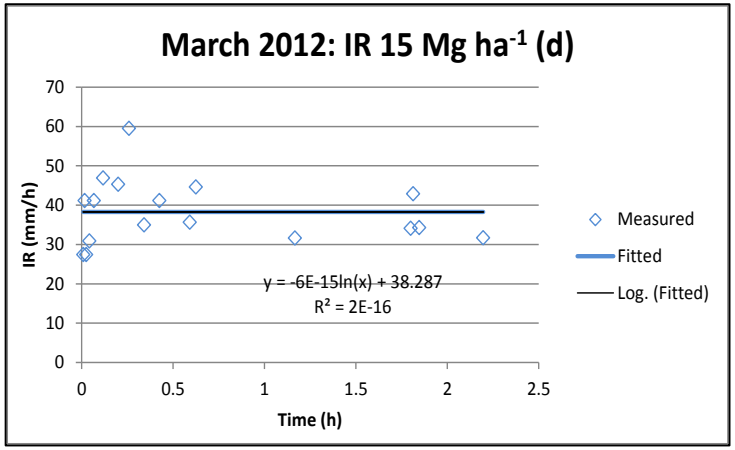


Appendix 5.4. Infiltration Curves Infiltration Rate Curves for March 2012, 2 months following FGD gypsum application: 15 Mg ha^{-1}

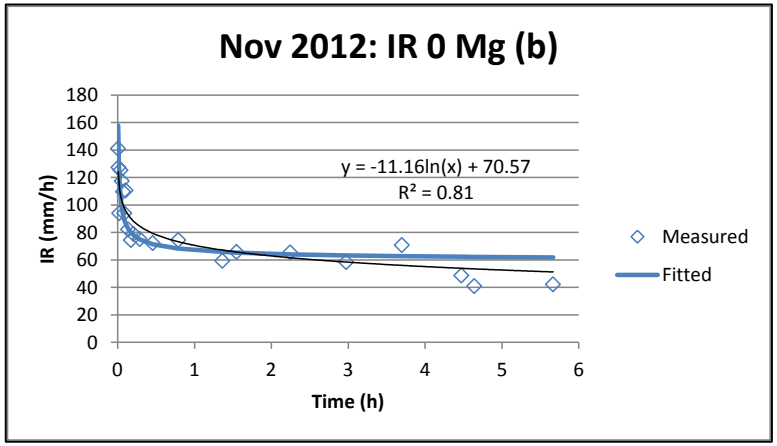


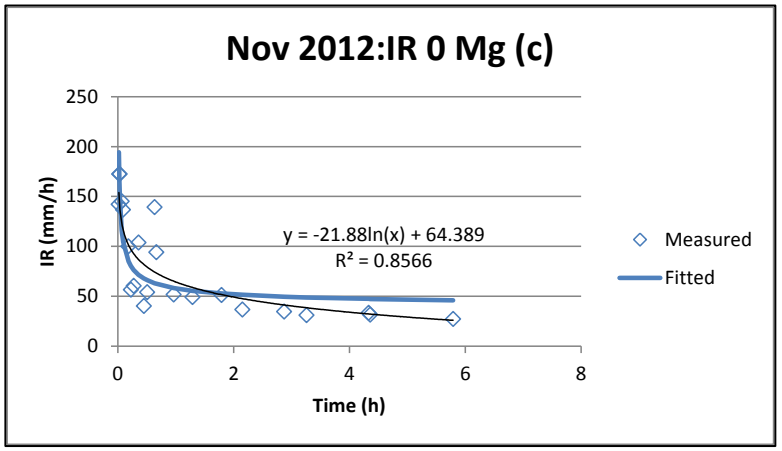


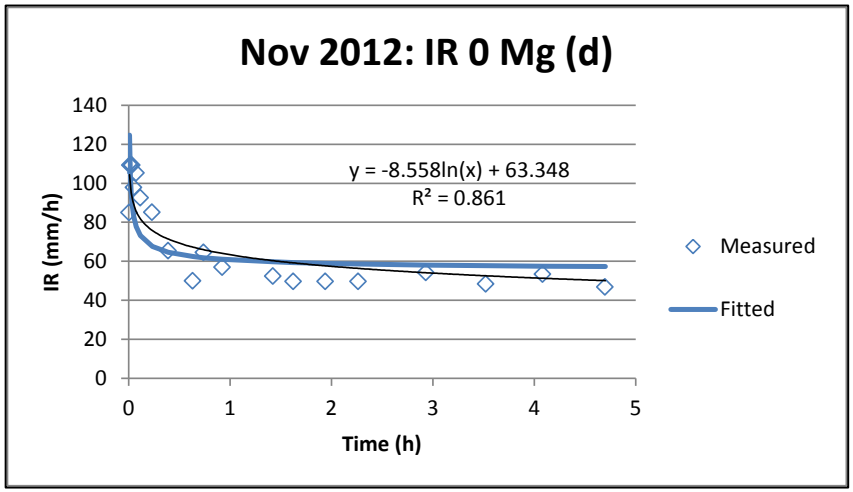




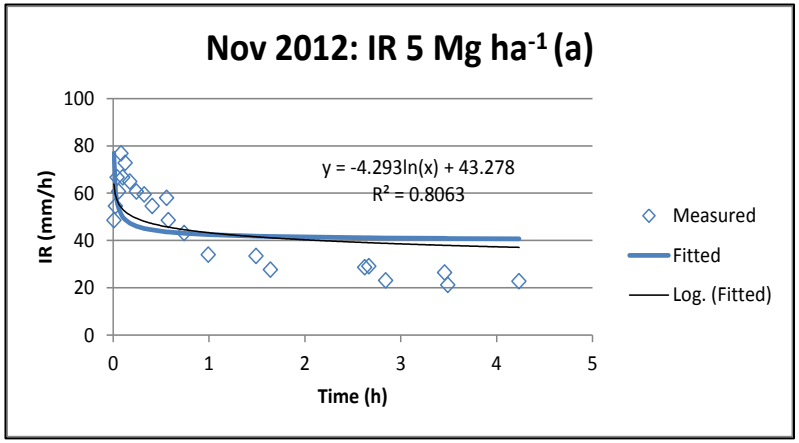
Appendix 5.5. Infiltration Rate Curves for November 2012, 10 months following FGD gypsum application: 0 Mg ha^{-1}

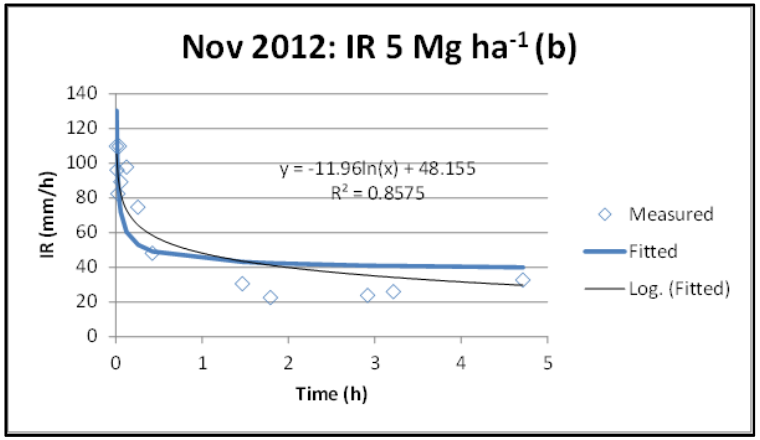


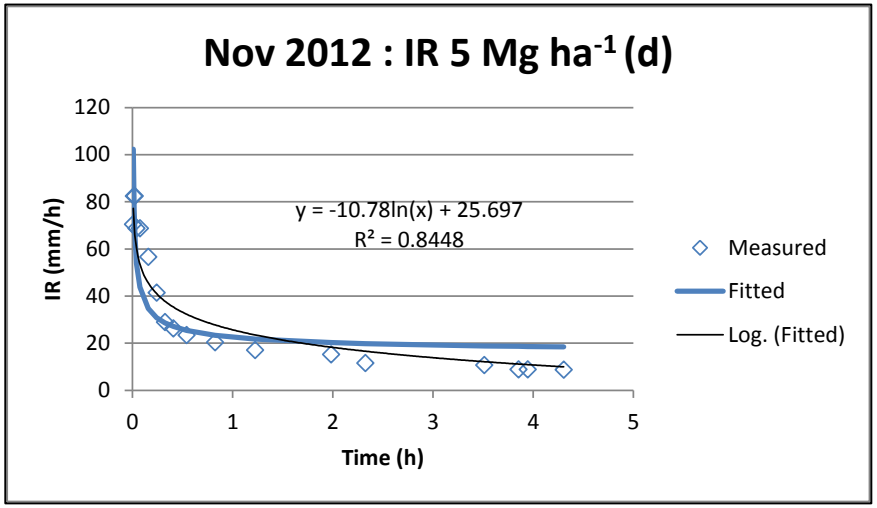




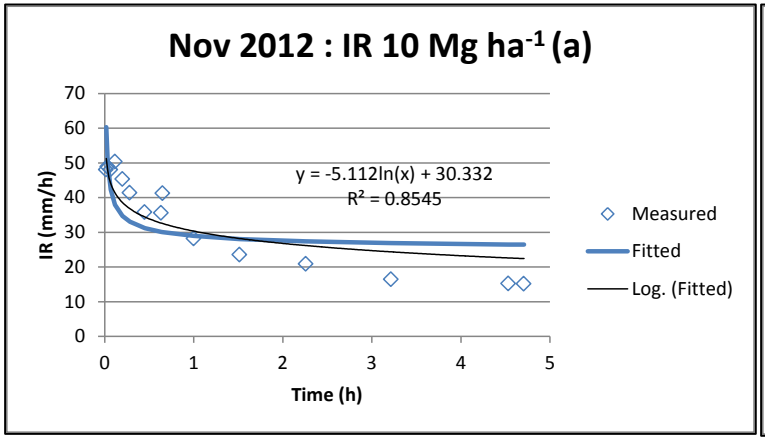
Appendix 5.6. Infiltration Rate Curves for November 2012, 10 months following FGD gypsum application: 5 Mg ha^{-1}

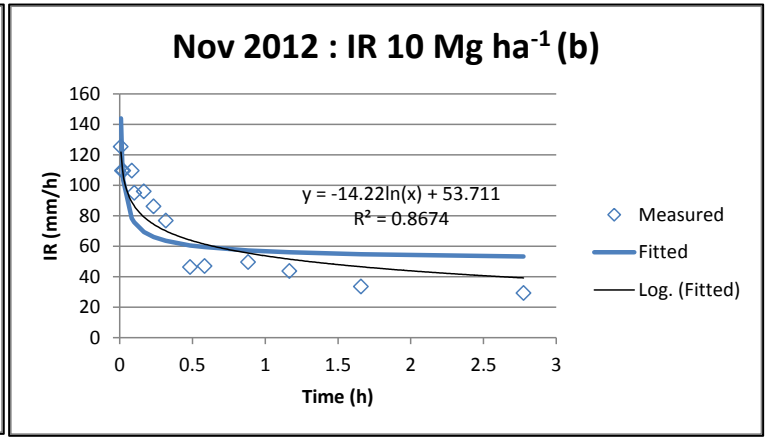


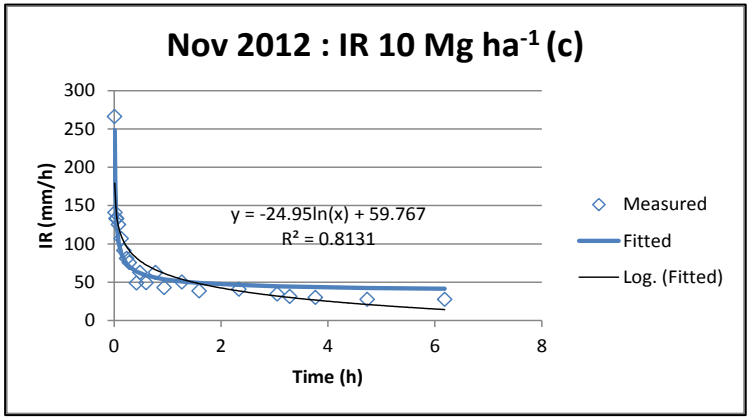


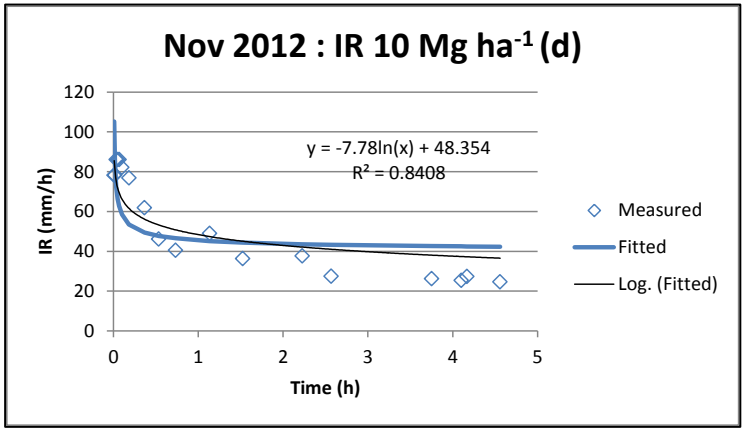


Appendix 5.7. Infiltration Rate Curves for November 2012, 10 months following FGD gypsum application: 10 Mg ha^{-1}

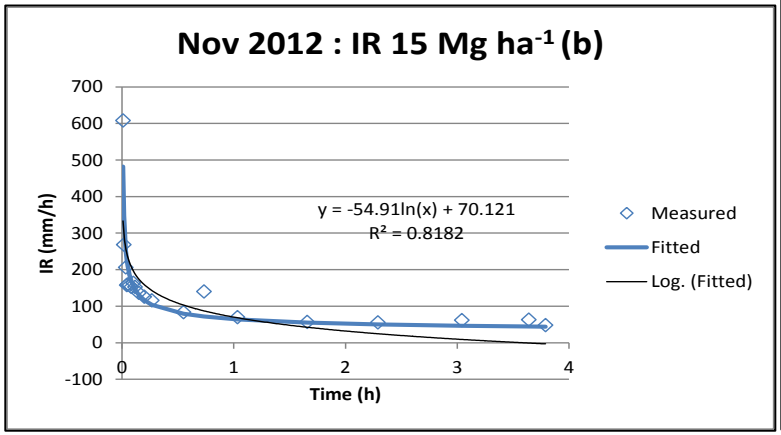


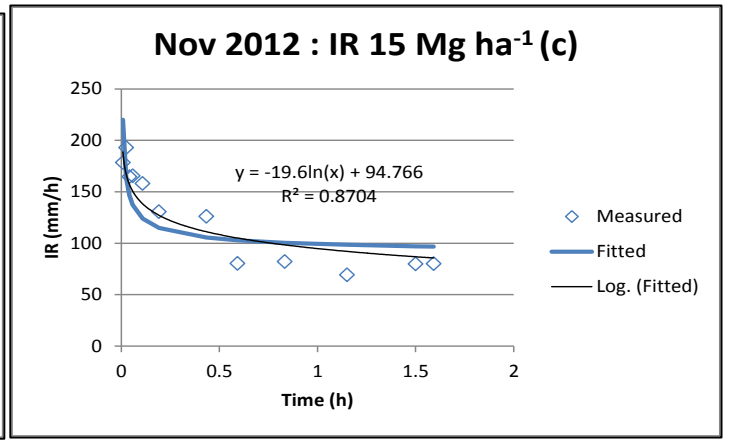


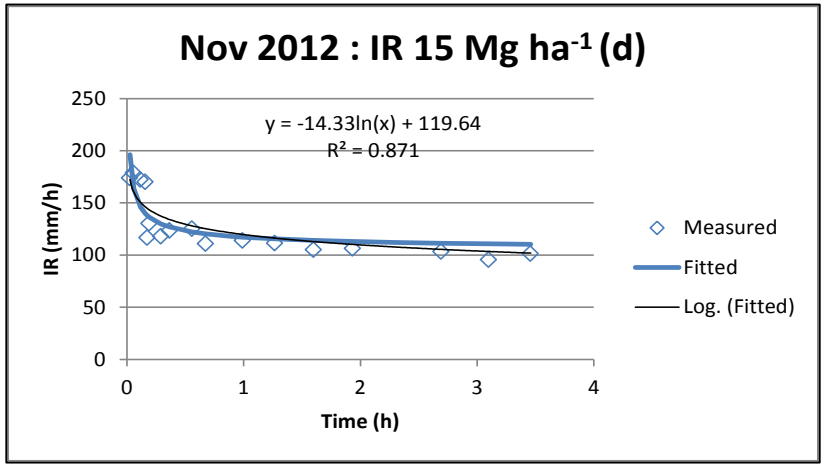




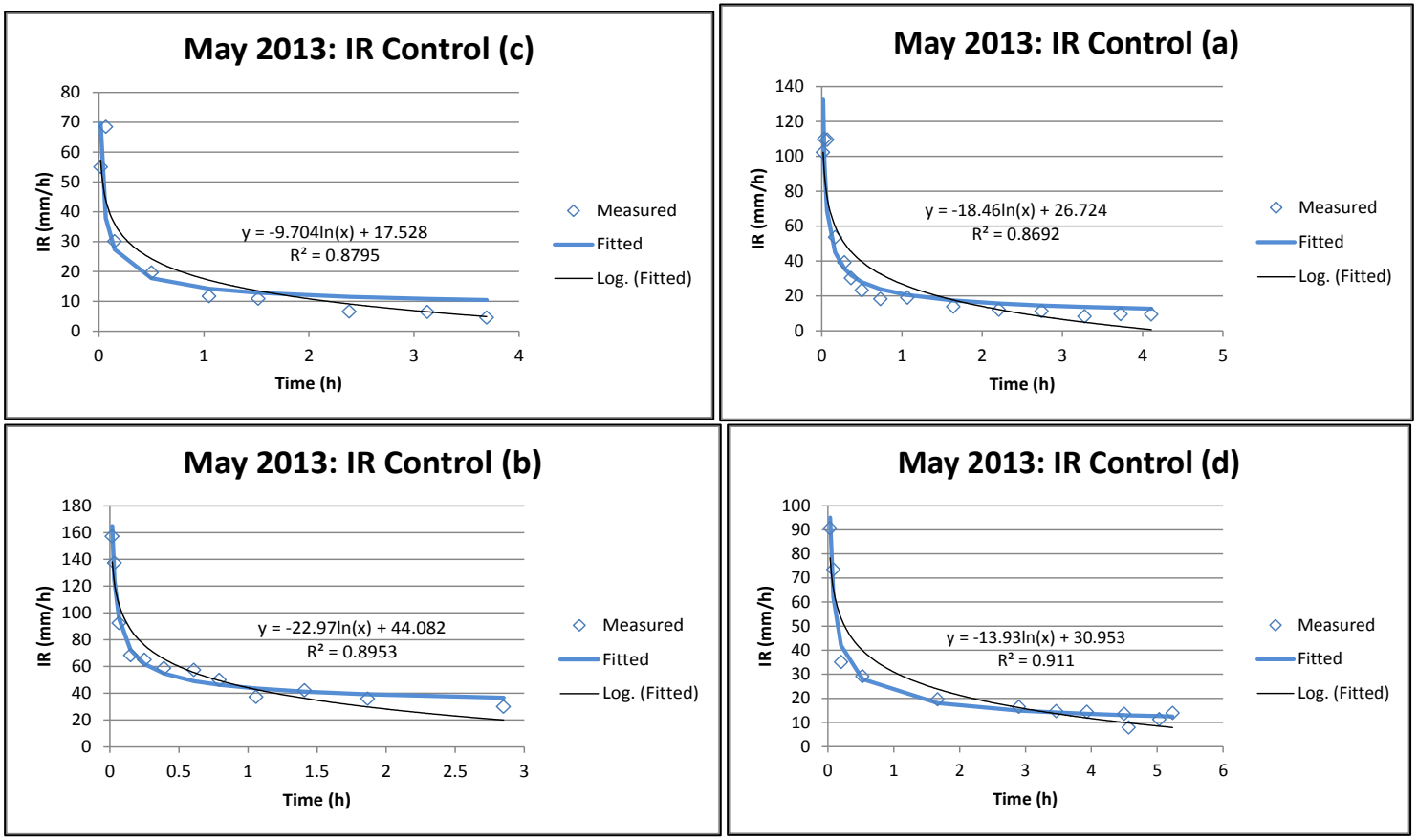
Appendix 5.8. Infiltration Rate Curves for November 2012, 10 months following FGD gypsum application: 15 Mg ha^{-1}



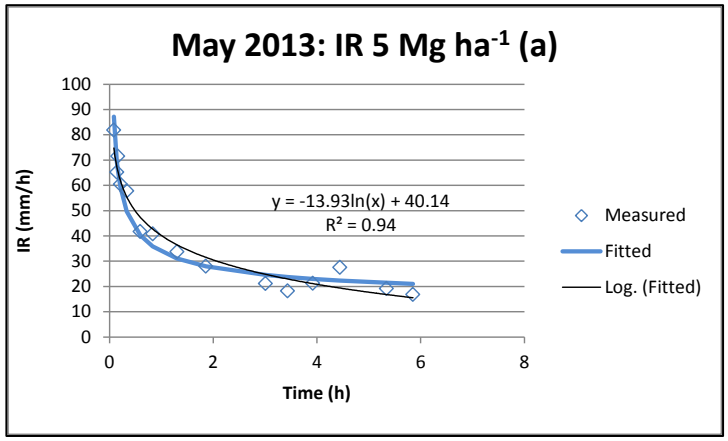


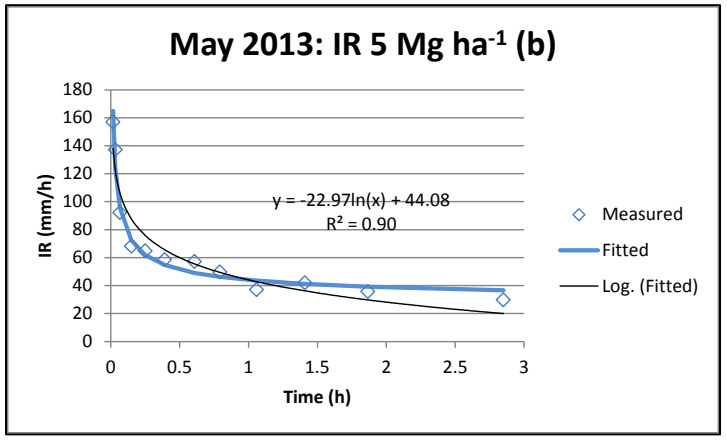


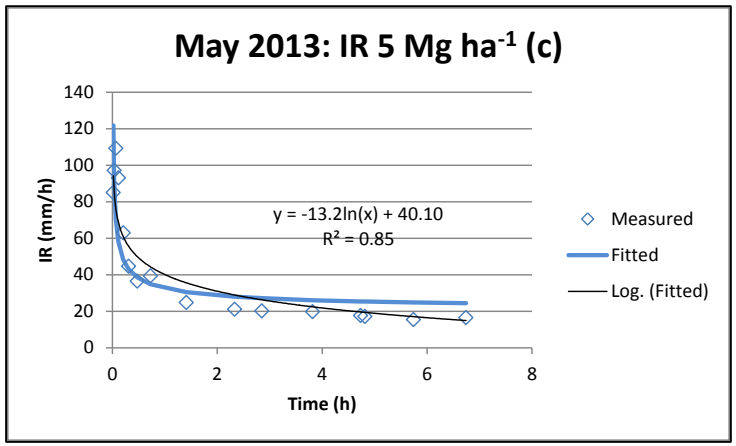
Appendix 5.9. Infiltration Rate Curves for May 2013, 16 months following FGD gypsum application: 0 Mg ha^{-1}

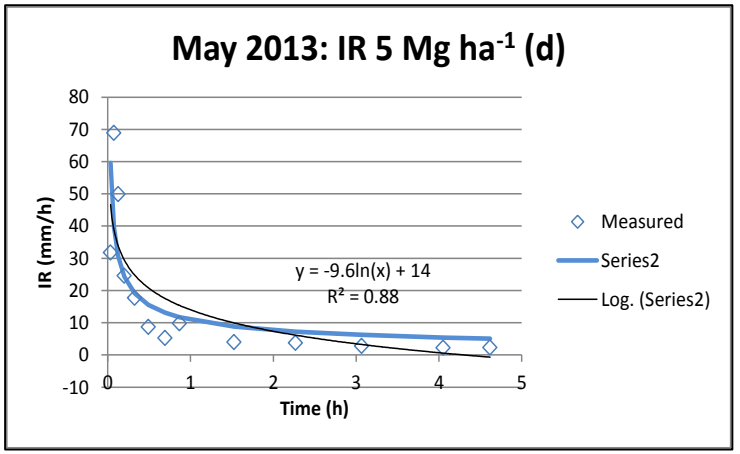


Appendix 5.10. Infiltration Rate Curves for May 2013, 16 months following FGD gypsum application: 5 Mg ha^{-1}

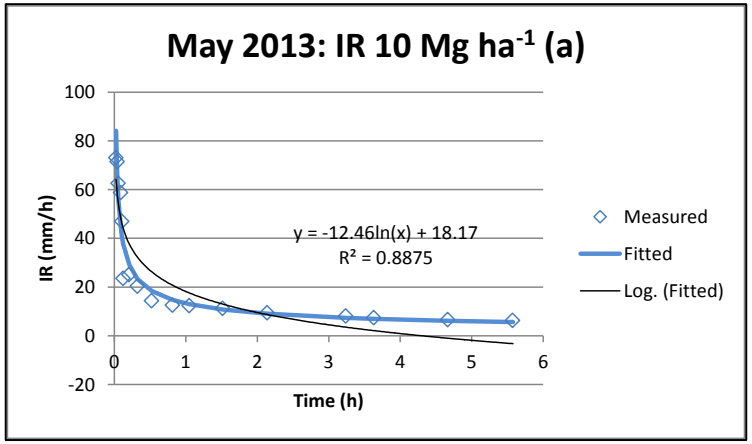


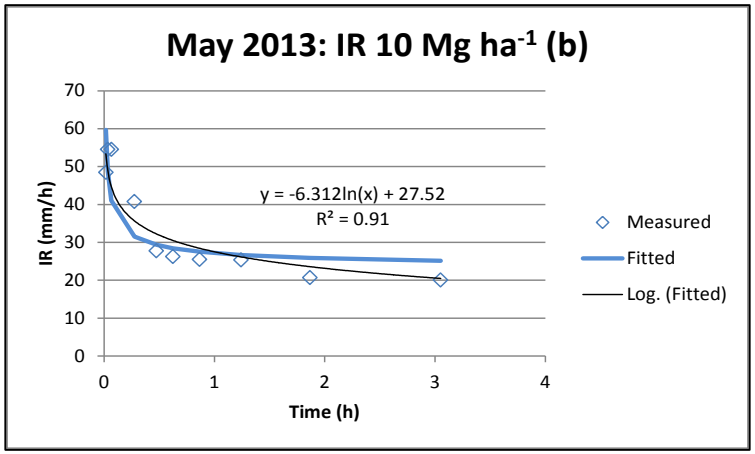


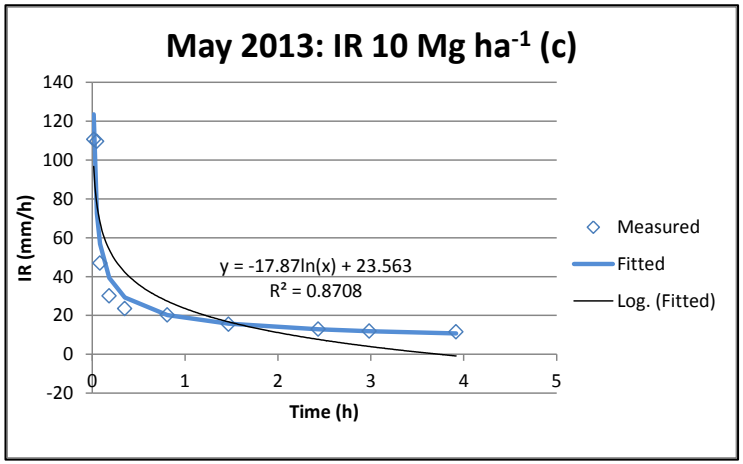


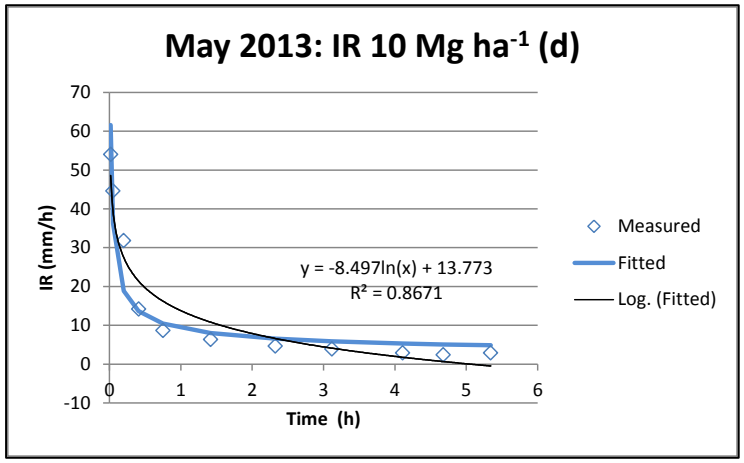


Appendix 5.11. Infiltration Rate Curves for May 2013, 16 months following FGD gypsum application: 10 Mg ha^{-1}

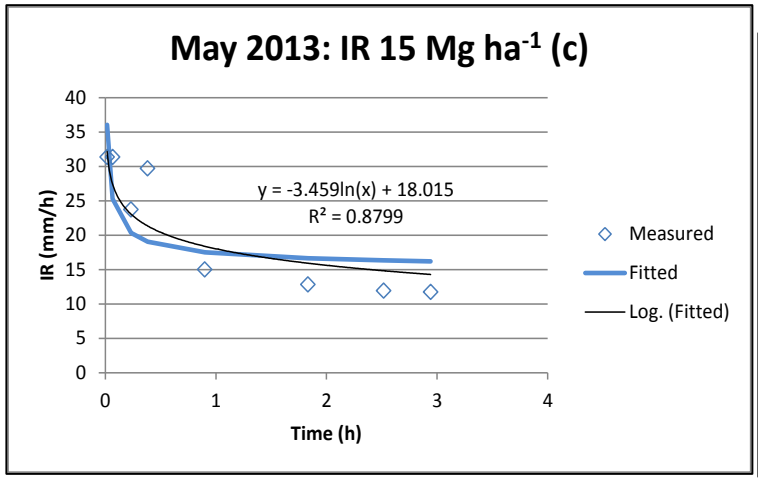


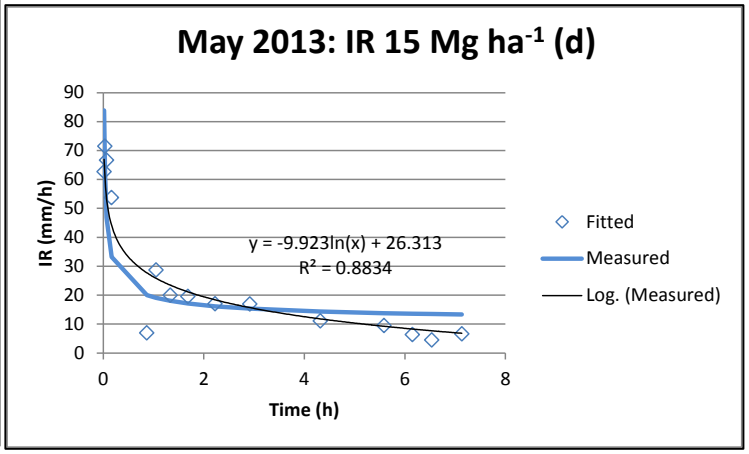


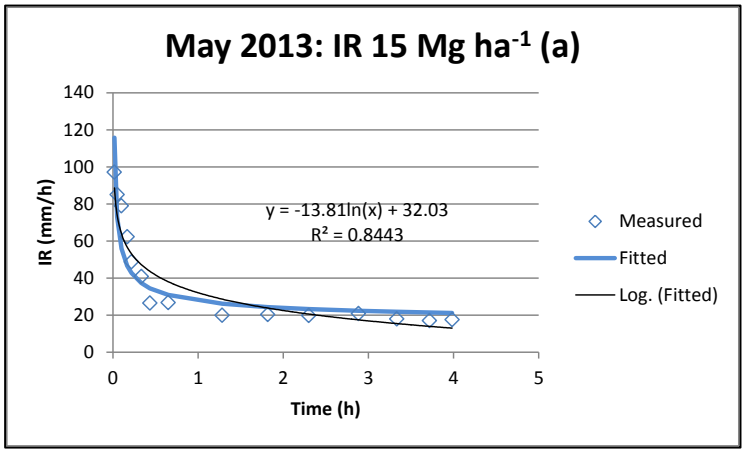


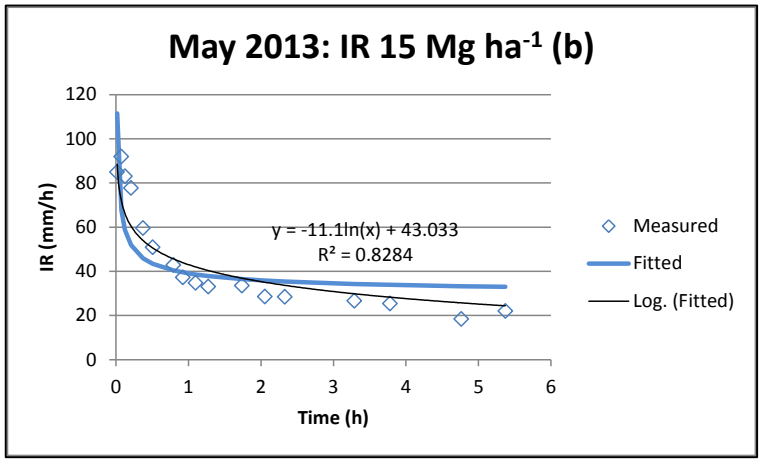


Appendix 5.12. Infiltration Rate Curves for May 2013, 16 months following FGD gypsum application: 15 Mg ha^{-1}



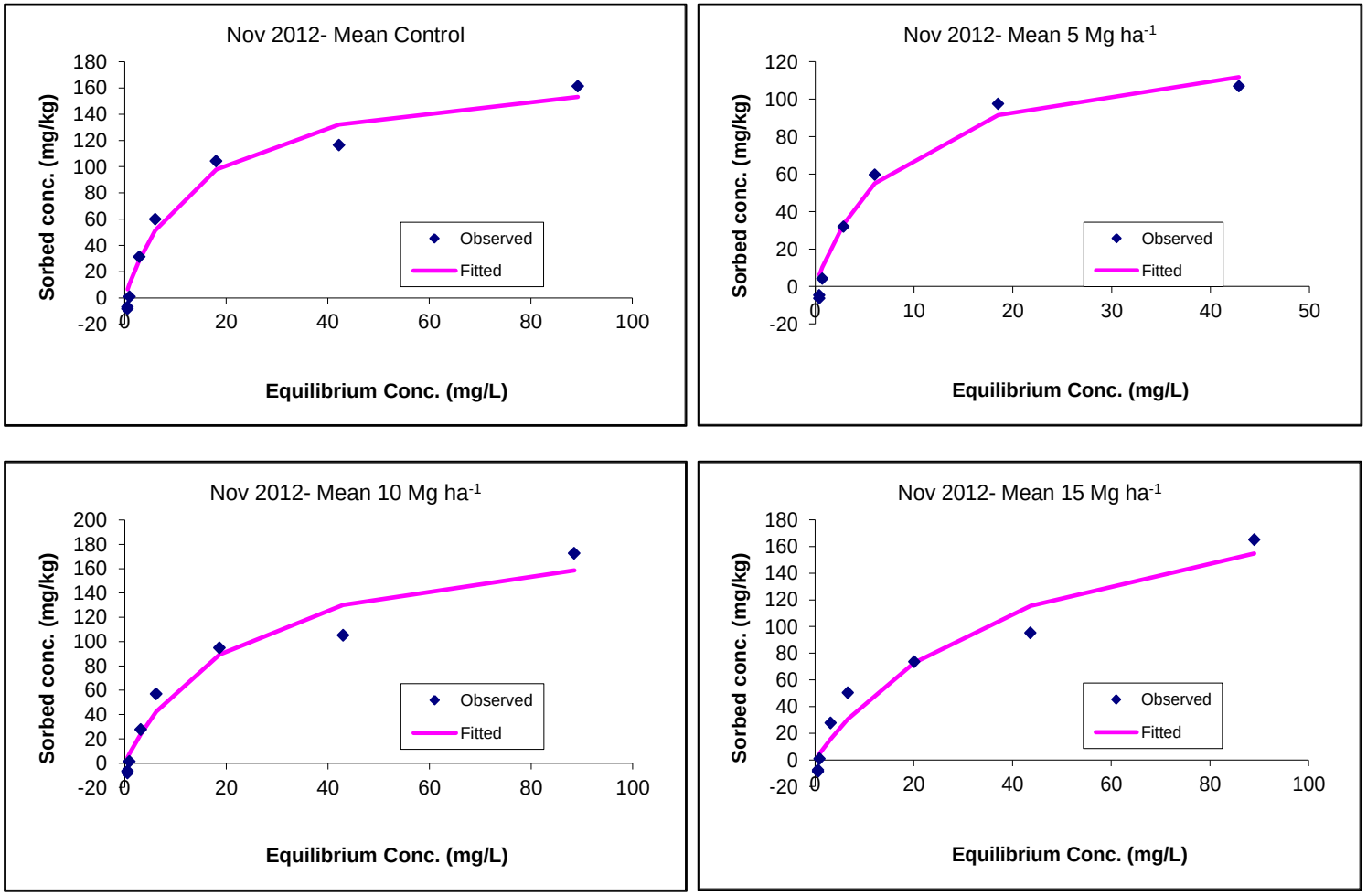






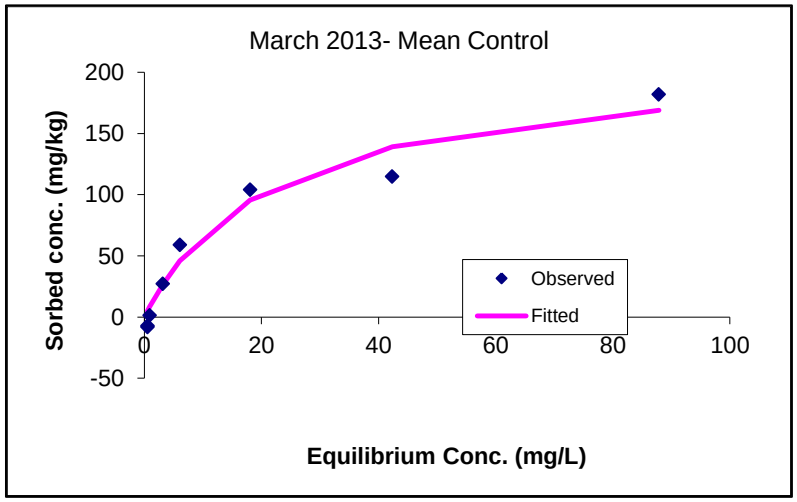
Appendix 6. P Sorption Curves – November 2012: Mean Equilibrium and Sorbed Concentrations for Each Treatment Level

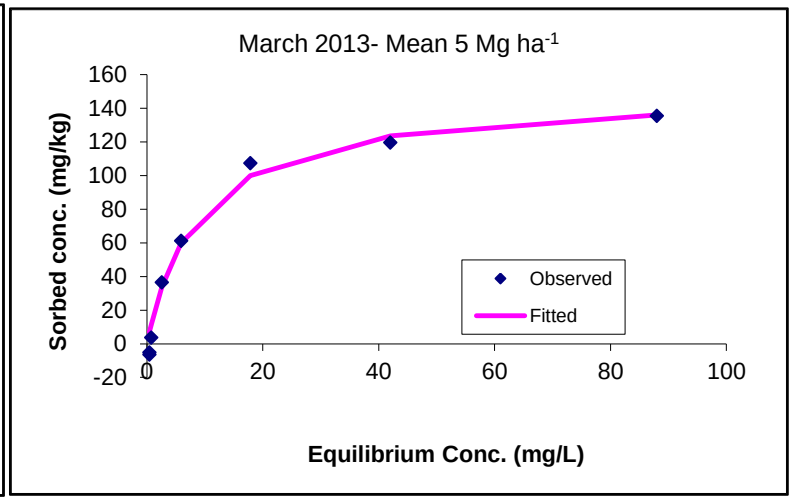
Based on Langmuir Worksheet provided by Carl Bolster (USDA-ARS, Bowling Green, KY -http://www.ars.usda.gov/pandp/docs.htm?docid=14971)

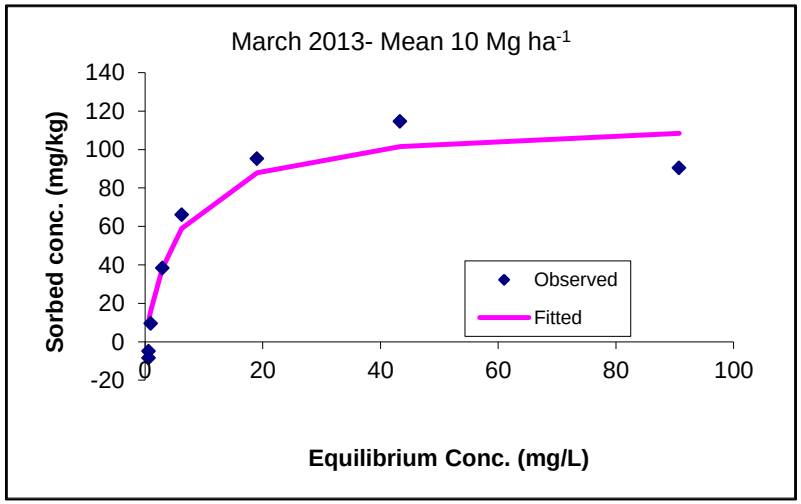


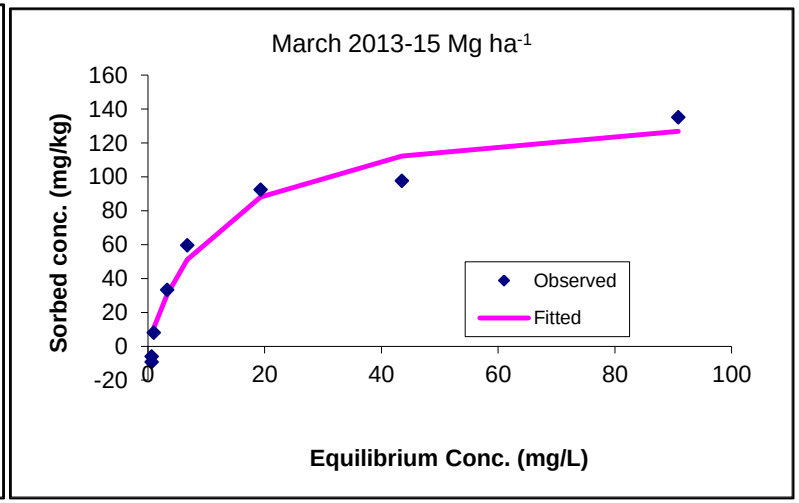
Appendix 6.2. P Sorption Curves – March 2013: Mean Equilibrium and Sorbed Concentrations for Each Treatment Level

Based on Langmuir Worksheet provided by Carl Bolster (USDA-ARS, Bowling Green, KY -http://www.ars.usda.gov/pandp/docs.htm?docid=14971)



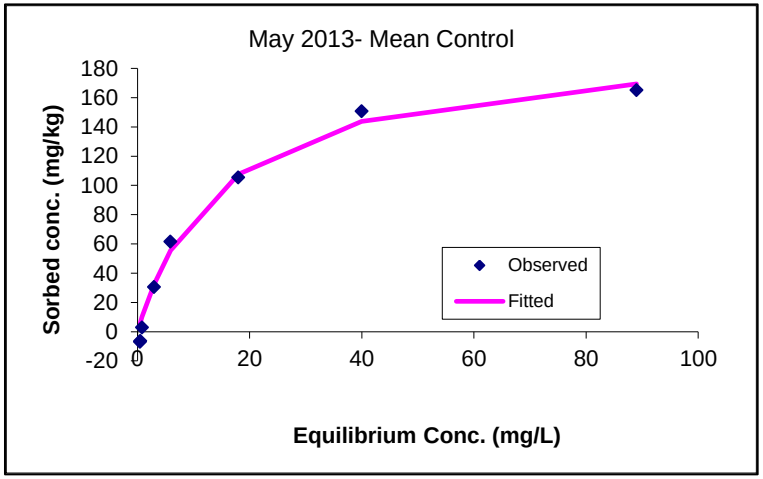


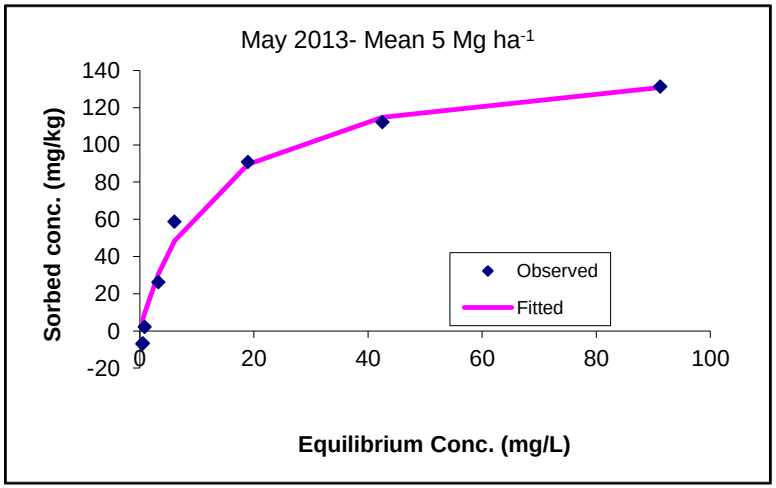


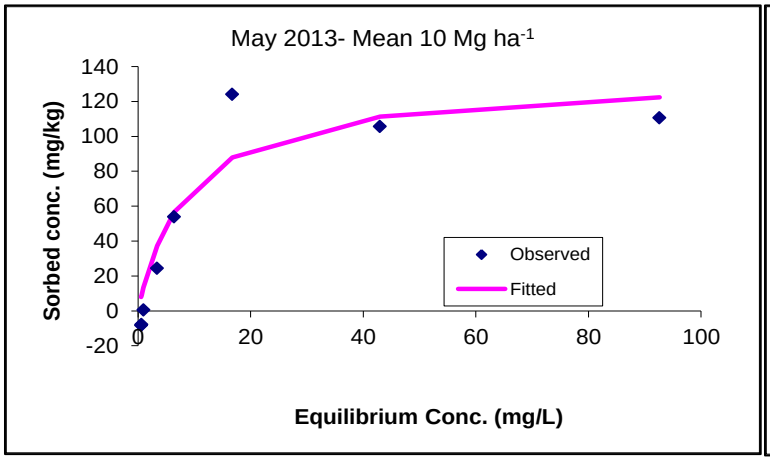


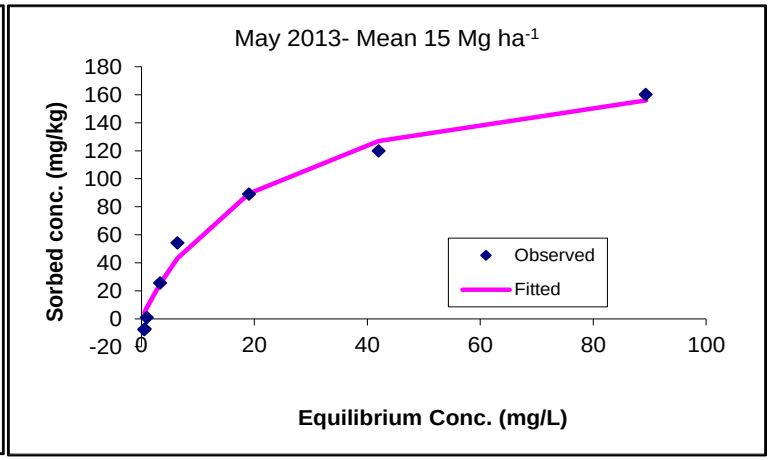
Appendix 6.2. P Sorption Curves – May 2013: Mean Equilibrium and Sorbed Concentrations for Each Treatment Level

Based on Langmuir Worksheet provided by Carl Bolster (USDA-ARS, Bowling Green, KY -http://www.ars.usda.gov/pandp/docs.htm?docid=14971)









Appendix 7. Alpha Values

Season	FGD Gypsum	Row	Al_{ox}	Fe_{ox}	P_{ox}	S max	S_{max}	P_{ox}+ S_{max}	α =
	Mg ha^{-1}		mmol kg^{-1}			mg kg^{-1}	mmol kg^{-1}	mmol kg^{-1}	(Pox+Smax)/ (Alox+Feox)
Nov '12	0	a	51.66	25.65	17.15	368.01	11.87	29.02	0.38
Nov '12	0	b	23.91	12.80	17.35	138.83	4.48	21.83	0.59
Nov '12	0	c	18.81	9.55	14.75	70.96	2.29	17.04	0.60
Nov '12	0	d	27.71	12.36	16.85	158.73	5.12	21.97	0.55
Nov '12	5	b	28.32	14.69	15.95	146.33	4.72	20.67	0.48
Nov '12	5	d	27.37	17.45	14.90	164.71	5.31	20.22	0.45
Nov '12	10	a	31.04	17.20	17.44	184.05	5.94	23.37	0.48
Nov '12	10	b	26.80	15.26	19.47	123.14	3.97	23.44	0.56
Nov '12	10	c	25.67	18.37	16.91	157.28	5.07	21.98	0.50
Nov '12	10	d	26.32	16.10	16.80	182.78	5.90	22.70	0.54
Nov '12	15	a	33.03	18.34	17.16	211.88	6.83	23.99	0.47
Nov '12	15	b	25.44	13.93	18.89	157.09	5.07	23.96	0.61
Nov '12	15	c	22.26	16.33	18.39	81.06	2.61	21.00	0.54
Nov '12	15	c2	21.46	15.57	17.00	151.50	4.89	21.89	0.59
Nov '12	15	d	27.16	13.57	15.71	230.71	7.44	23.15	0.57
Mar '13	0	a	43.25	23.11	13.65	366.40	11.82	28.82	0.43
Mar '13	0	b	24.42	12.29	16.19	143.74	4.64	20.34	0.55
Mar '13	0	c	18.19	8.80	14.47	217.38	7.01	20.66	0.77
Mar '13	0	d	26.82	10.98	15.88	130.68	4.22	20.40	0.54
Mar '13	5	a	29.20	11.36	13.70	184.59	5.95	20.42	0.50
Mar '13	5	b	27.61	13.27	14.79	123.64	3.99	19.87	0.49
Mar '13	5	c	26.92	16.29	15.12	172.57	5.57	19.26	0.45
Mar '13	5	d	24.50	15.43	14.16	212.33	6.85	21.63	0.54
Mar '13	10	a	28.91	16.23	15.26	199.58	6.44	21.56	0.48
Mar '13	10	b	25.40	14.66	19.30	150.02	4.84	19.00	0.47
Mar '13	10	c	23.80	17.04	16.53	110.43	3.56	18.82	0.46
Mar '13	10	d	25.74	15.92	16.27	150.19	4.84	24.14	0.58
Mar '13	15	a	31.75	18.15	17.00	161.51	5.21	21.74	0.44
Mar '13	15	b	25.49	13.64	17.94	154.84	4.99	21.27	0.54
Mar '13	15	c	20.36	16.39	16.83	178.00	5.74	22.74	0.62
Mar '13	15	d	27.32	13.59	16.12	187.37	6.04	23.99	0.59
May '13	0	a	41.52	23.52	14.95	306.91	9.90	26.73	0.41
May '13	0	b	23.02	11.30	15.79	235.42	7.59	23.71	0.69
May '13	0	c	19.91	10.12	14.26	108.97	3.52	18.47	0.62
May '13	0	d	25.91	10.58	14.59	157.88	5.09	20.88	0.57
May '13	5	a	28.70	12.78	14.13	187.69	6.05	20.31	0.49
May '13	5	b	27.24	14.22	16.50	122.04	3.94	18.53	0.45

May '13	5	c	24.89	18.45	15.43	153.44	4.95	19.08	0.44
May '13	5	d	23.42	15.18	14.04	133.58	4.31	20.81	0.54
May '13	10	a	29.95	18.05	17.04	189.00	6.10	21.52	0.45
May '13	10	b	25.09	14.88	20.28	117.91	3.80	17.84	0.45
May '13	10	c	23.15	16.08	17.12	137.54	4.44	21.48	0.55
May '13	10	d	24.72	15.63	14.77	141.17	4.55	24.84	0.62
May '13	15	a	29.89	15.93	15.19	230.17	7.42	24.54	0.54
May '13	15	c	18.83	14.82	14.66	139.76	4.51	19.28	0.57
May '13	15	d	23.15	12.25	14.21	118.26	3.81	19.00	0.54

Appendix 8. M3, Ammonium Oxalate and DPS values

Season	FGD Gypsum	Row	WEP	Al_{ox}	Fe_{ox}	P_{ox}	DPS_{ox} calc alpha	DPS_{ox} α = 0.5	M3-Al	M3-Fe	M3-P	M3-PSR P/(Al+Fe)
	Mg ha^{-1}		mg kg^{-1}						mg kg^{-1}			
Fall '12	0	a	8.94	1394.81	1436.30	531.64	59.09	44.37	1476.58	318.56	315.58	0.17
Fall '12	0	b	17.39	645.62	716.81	537.86	75.06	94.52	782.33	359.95	452.21	0.41
Fall '12	0	c	14.89	507.91	534.91	457.36	90.83	104.03	694.95	317.01	369.06	0.38
Fall '12	0	d	14.39	748.25	692.02	522.47	76.70	84.12	842.85	320.22	388.03	0.34
Fall '12	5	b	11.40	764.76	822.83	494.52	77.17	74.17	866.87	296.50	357.73	0.31
Fall '12	5	d	9.38	739.12	977.05	461.97	73.72	66.49	747.98	349.58	315.10	0.30
Fall '12	10	a	11.19	838.06	963.27	540.50	74.60	72.29	958.02	380.74	364.74	0.28
Fall '12	10	b	14.50	723.73	854.56	603.58	83.06	92.57	723.54	366.79	476.00	0.46
Fall '12	10	c	8.25	692.99	1028.70	524.07	76.92	76.78	719.96	362.60	370.29	0.36
Fall '12	10	d	8.57	710.58	901.53	520.83	74.02	79.22	736.11	367.74	368.20	0.35
Fall '12	15	a	6.26	891.76	1026.78	531.85	71.51	66.80	988.49	321.65	363.36	0.28
Fall '12	15	b	9.52	686.93	780.17	585.57	78.85	95.95	722.49	356.20	454.46	0.44
Fall '12	15	c	13.59	601.15	914.53	570.06	87.55	95.29	750.19	378.14	410.66	0.38
Fall '12	15	c2	12.99	579.31	871.81	527.06	77.67	91.84	747.83	372.87	393.09	0.37
Fall '12	15	d	12.40	733.22	759.72	486.88	67.85	77.14	767.32	329.92	365.56	0.34
March '13	0	a	3.58	1167.68	1294.32	423.00	47.34	41.12	1428.45	276.61	216.20	0.12
March '13	0	b	17.99	659.23	688.40	501.81	79.57	88.19	778.07	357.13	419.66	0.38
March '13	0	c	14.30	491.13	492.54	448.46	70.03	107.22	704.83	314.18	342.46	0.35
March '13	0	d	17.99	724.25	614.92	492.39	77.85	84.03	879.33	329.02	411.87	0.35
March '13	5	a	8.39	788.28	635.92	424.63	67.08	67.56	1068.58	329.43	314.07	0.22
March '13	5	b	11.60	745.42	743.36	458.34	55.26	72.33	979.85	317.00	408.00	0.31
March '13	5	c	12.49	726.75	912.14	468.72	78.49	69.99	855.25	326.13	356.37	0.31
March '13	5	d	7.69	661.41	864.06	439.02	65.46	70.94	860.99	398.01	360.60	0.30
March '13	10	a	10.30	780.62	908.95	472.93	70.77	67.59	1076.05	397.09	385.58	0.26
March '13	10	b	16.60	685.69	820.99	598.21	101.56	96.35	822.46	382.30	519.47	0.45
March '13	10	c	8.27	642.61	953.99	512.52	87.86	80.97	832.41	392.74	421.57	0.36
March '13	10	d	8.23	694.91	891.67	504.51	67.41	78.13	795.34	381.95	384.97	0.34

March '13	15	a	6.44	857.32	1016.15	526.93	78.17	68.13	1134.75	395.89	396.73	0.26
March '13	15	b	12.99	688.13	763.87	556.25	84.36	91.72	877.92	383.37	490.85	0.40
March '13	15	c	10.80	549.71	917.71	521.80	74.02	91.61	720.82	365.71	414.49	0.40
March '13	15	d	15.00	737.63	761.22	499.64	67.19	78.79	876.55	365.83	396.93	0.33
May '13	0	a	10.20	1121.04	1316.89	463.51	55.93	45.98	1224.46	289.12	305.28	0.19
May '13	0	b	17.80	621.42	633.01	489.36	66.57	91.99	798.79	324.04	413.68	0.38
May '13	0	c	14.09	537.54	566.61	442.05	77.22	94.98	716.33	320.96	318.43	0.32
May '13	0	d	12.20	699.65	592.34	452.24	69.87	79.96	853.77	315.91	310.41	0.27
May '13	5	a	11.80	774.83	715.48	438.13	69.57	68.15	1017.80	320.73	341.40	0.25
May '13	5	b	14.19	735.46	796.50	511.42	85.08	79.58	834.37	325.92	397.04	0.35
May '13	5	c	15.70	672.09	1033.29	478.19	80.83	71.18	770.43	341.54	366.70	0.34
May '13	5	d	10.10	632.43	850.21	435.24	67.48	72.74	783.89	337.82	309.58	0.28
May '13	10	a	10.90	808.57	1010.92	528.33	79.19	71.01	941.60	375.88	360.19	0.28
May '13	10	b	16.30	677.40	833.30	628.83	113.68	101.50	762.08	381.09	530.29	0.49
May '13	10	c	13.90	624.95	900.36	530.69	79.70	87.29	747.63	380.60	523.67	0.49
May '13	10	d	5.86	667.46	875.54	457.86	59.46	73.20	795.43	355.60	424.54	0.38
May '13	15	a	7.98	807.12	892.16	470.80	61.88	66.28	1005.01	320.31	363.65	0.27
May '13	15	b	9.07	597.63	685.77	504.81			768.94	351.39	423.23	0.39
May '13	15	c	9.91	508.45	830.05	454.52	76.06	87.13	745.70	383.54	371.82	0.35
May '13	15	d	14.60	625.03	686.26	440.62	59.03	80.29	717.56	340.36	349.05	0.34

Appendix 9. Total Sulfur Data

FGD Gypsum (Mg ha^{-1})	Row	Depth (cm)	Total S (mg kg^{-1})	Mean Error	FGD Gypsum (Mg ha^{-1})	Row	Depth (cm)	Mean	Mean Error
0	a	15	201	±10	**10**	a	15	551	±109
0	b	15	199	±13	**10**	b	15	253	±19
0	c	15	161	±5	**10**	c	15	507	±226
0	d	15	188	±6	**10**	d	15	1040	±301
0	a	30	191	±18	**10**	a	30	275	±18
0	b	30	164	±17	**10**	b	30	201	±38
0	c	30	140	±20	**10**	c	30	275	±35
0	d	30	147	±3	**10**	d	30	261	±29
0	a	61	107	±28	**10**	a	61	143	±19
0	b	61	157	±25	**10**	b	61	273	±20
0	c	61	181	±13	**10**	c	61	154	±26
0	d	61	247	±27	**10**	d	61	192	±10
0	d	91	111	±43	**10**	d	91	137	±26
5	a	15	206	±12	**15**	a	15	714	±223
5	b	15	211	±26	**15**	b	15	712	±149
5	c	15	185	±9	**15**	c	15	592	±206
5	d	15	226	±24	**15**	d	15	266	±26
5	a	30	238	±37	**15**	a	30	346	±19
5	b	30	201	±13	**15**	b	30	261	±18
5	c	30	160	±27	**15**	c	30	241	±15
5	d	30	223	±14	**15**	d	30	260	±23
5	a	61	178	±16	**15**	a	61	177	±63
5	b	61	104	±22	**15**	b	61	198	±28
5	c	61	133	±22	**15**	c	61	229	±28
5	d	61	159	±28	**15**	d	61	269	±36
5	d	91	112	±25	**15**	d	91	147	±14

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